AFAPL-TR-77-12

ADA042558

HIGH ENERGY DENSITY PELLETIZED ALUMINUM CHLORINE THERMAL BATTERIES

EUREKA ADVANCE SCIENCE CORPORATION
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APRIL 1977

TECHNICAL REPORT AFAPL-TR-77-12
FINAL REPORT FOR PERIOD 15 MAY 1976 - 15 DECEMBER 1976

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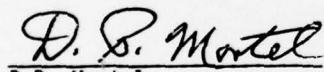
This final report was submitted by Eureka Advance Science Coropration, under Contract F33615-76-C-2080. The effort was sponsored by the Air Force Aero Propulsion Laboratory, Air Force Systems Command, Wright-Patterson AFB, Ohio under Project 3145, Task 314522 and Work Unit 31452271 with W.S. Bishop/ POE-1 as *Project Engineer In-Charge.* Mr. David M. Ryan of Eureka Advance Science Corporation was technically responsible for the work.

This report has been reviewed by the Information Office, (ASD/OIP) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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FOR THE COMMANDER

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AIR FORCE - 28 JUN 77 - 225

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFAPL-TR-77-12	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) High Energy Density Pelletized Aluminum Chlorine Thermal Batteries.		5. TYPE OF REPORT & PERIOD COVERED Final Report, 15 May 76 to 15 Dec 76.
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) David M. Ryan and L. C. Bricker		8. CONTRACT OR GRANT NUMBER(s) F33615-76-C-2080 new
9. PERFORMING ORGANIZATION NAME AND ADDRESS Eureka Advance Science Corporation P.O. Box 1547 Bloomington, Illinois 61701		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62203F, 3145, 314522, 31452271
11. CONTROLLING OFFICE NAME AND ADDRESS AFAPL/POE-1 WPAFB, OH 45433		12. REPORT DATE 15 April 1977
		13. NUMBER OF PAGES 114
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) SAME		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE N/A

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release;
distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Distribution is Unlimited

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Thermal Batteries, Molten Salt Batteries, Aluminum Chlorine Batteries,
Batteries, Primary Batteries, Reserve Batteries, Automatically Activated
Batteries

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The Eureka Advance Science Corporation entered into a contract to
engineer the development of a thermal battery based upon an electrochemical
cell developed at the Frank J. Seiler Research Laboratory. This cell utilizes
aluminum or lithium-aluminum alloy as its anode, a Cab-O-Sil/NaAlCl$_4$ mixture
as anolyte, and a mixture of anolyte, MoCl$_5$ and graphite as cathode.
Engineering research at the Eureka Advance Science Corporation was undertaken
to develop a profile of the operating characteristics of a battery utilizing

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this cell, and to investigate the feasibility of manufacturing such a battery.

Commercially available $NaAlCl_4$ was found to be unsuitable for cell preparation. The synthesis of $NaAlCl_4$ was carried out at FJSRL and at Eureka, and both synthesized materials were found satisfactory for the production of anolyte and catholyte. Lithium-aluminum alloys of 20 w/o Li and 28 w/o Li were investigated, and both were found to be suitable anode materials.

The operating characteristics of the cell described by FJSRL were successfully reproduced, and experimentation was carried out to further improve the cell. Four cell variables were subjected to a factorial design analysis to provide data for construction of cells for optimum performance.

Two heat source materials were investigated for use in the thermal batteries; $Zr/BaCrO_4$ and $Fe/KClO_4$. Both were found satisfactory, but the $Fe/KClO_4$ provided the better overall battery performance.

The total functionality of a thermal battery utilizing these cells was demonstrated by the performance of a 28 volts 2 amp battery operating over the temperature range of -65°F to +165°F. These batteries have comparatively long life and high energy density capabilities, and the skin temperature of the battery is ordinarily low enough that it can be held in the hand. Batteries of this design appear to present an excellent manufacturing potential.

FOREWORD

This report describes the exploratory development conducted by Eureka Advance Science Corporation personnel at their Bloomington, Illinois facilities on a high energy density pelletized aluminium chlorine thermal battery under contract (Contract No. F33615-76-C-2080) with the U.S. Air Force Aero Propulsion Laboratory located at Wright-Patterson Air Force Base, Ohio. This work was based on basic research work conducted by personnel of the Air Force Frank J. Seiler Research Laboratories, U.S. Air Force Academy, Colorado and was for the purpose of determining if a practical aluminium chlorine thermal battery could be demonstrated using the results of the above basic research.

Submitted date for this report was March 1977, covering effort completed during the interval 15 May 1976 thru 15 Dec 1976.

The cognizant Air Force project officer was Mr. W.S. Bishop, AFAPL/POE-1, Wright-Patterson Air Force Base, Ohio. The technical support rendered by Mr. R.A. March of the project officer's organization was very beneficial and greatly appreciated. The consultation and technical support of Lt. Col. Lowell King, Capt. John Erbacher, and Lt. Chuck Hussey of the Air Force Frank J. Seiler, Air Force Academy, Colorado was outstanding and a major contribution to the program success.

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SECTION I

INTRODUCTION

In 1950 the Eureka Advance Science Corporation was known as the Product Engineering Department of the Eureka Williams Corporation. During the Korean War, Eureka contributed to the war effort by putting into production a thermal battery used in the 81mm Mortar Proximity Fuze. The battery was designed by an independent research corporation who did not have the facilities or experience to manufacture anything in large quantities. In 1953 work was started with the then, Naval Ordnance Laboratory, Silver Spring, Maryland, on a battery for a universal Proximity Fuze to go on all rotating projectiles. The design of these fuzes led to the development of the Pressed Pellet Thermal Battery by the Eureka Williams Corporation. Today this type of thermal battery construction is universally used by all thermal battery manufacturers.

Frank J. Seiler Research Laboratory (FJSRL), established at the Air Force Academy, Colorado Springs, Colorado, in 1964, started work on the electrochemistry of molten salt electrolytes, in particular the $AlCl_3/NaCl$ system, shortly after establishment. In 1970 FJSRL received a patent for the concentration cell based on this electrolyte system. As improvements were made more patents were issued and in 1971 the first formation cell was made. Work was done to improve this system and as a result of this work a three layered pelletized thermal cell was developed.

In the spring of 1976 the Eureka Advance Science Corporation entered into a contract to engineer the development of thermal batteries based on the work done at FJSRL. It was not known at that time if such a thermal battery could be built.

The first problem encountered at Eureka was the lack of large amounts of electrolyte. $NaAlCl_4$ had to be synthesized and mixed with Cab-O-Sil. Most of the $NaAlCl_4$ used in this contract was supplied by FJSRL.

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Once a supply of electrolyte was available work was started to reproduce the cell made at FJSRL. This cell was described in a correspondence from that facility. This was a three layer pelletized cell with the following construction.

ITEM	WEIGHT
1) Anode:	
90 ^{W}/o NaAlCl$_4$/10 ^{W}/o Cab-O-Sil*	0.50 gram
48 atom % LiAl Alloy	0.50 gram
2) Separator (Anolyte)	
NaAlCl$_4$ 90/10 Mix	0.90 gram
3) Cathode (Catholyte)	
NaAlCl$_4$ 90/10 Mix	0.45 gram
MoCl$_5$	0.50 gram
Graphite	0.16 gram
Total Weight	3.01 gram

This cell was tested at a temperature of 175°C and at a constant current of 15 mA/cm^2 between heated platens. After this cell was reproduced the cell components were varied and experimented with and an optimum cell was designed.

Other problems were encountered when battery construction began. It was found that the production methods used to make other thermal batteries could not be used for batteries made with the NaAlCl$_4$ electrolyte, the LiAl Anode or the MoCl$_5$ graphite catholyte. Alternative methods had to be found.

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*This mixture shall be called NaAlCl$_4$ 90/10 mix for the remainder of this report.

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The first batteries were made with a zirconium/barium chromate heat source. The final batteries were built with an iron/potassium perchlorate heat source. The iron heat source material was supplied courtesy of Sandia Research Laboratories at Albuquerque, New Mexico.

As a result of the work done by Eureka it was proven that a successful thermal battery could be made with the electrochemical system developed by FJSRL. It was demonstrated that a 28 volt, 2 amp battery was a realistic goal for a fully engineered battery. It was also demonstrated that lifetimes in excess of half an hour and current densities in excess of 350 mA/cm^2 were realistic goals for a fully engineered battery. This work has shown that the $Al/NaAlCl_4/MoCl_5,C$ system is a good electrochemical system and that further work should be done to fully engineer this battery.

SECTION II

EXPERIMENTAL RESULTS AND DISCUSSION

MATERIALS

All cell component materials were handled in a "dry room" at approximately 2.5% relative humidity (27°C) or in an inert atmosphere box under dry argon.

ANODE

Lithium-aluminum alloy (20 ^{W}/o and 28 ^{W}/o Li) were ordered from Foote Mineral Company. Initially some anodes were made by mixing LiAl alloy with anolyte. As these anodes did not give better performance than those made from pure LiAl alloy, the practice of mixing anolyte with the alloy was abandoned.

ANOLYTE

The anolyte material was composed of sodium tetrachloroaluminate ($NaAlCl_4$) mixed with either purified kaolin or "Cab-O-Sil" in varying amounts.

$NaAlCl_4$

$NaAlCl_4$ from three different sources was investigated: a commercial grade of $NaAlCl_4$ from City Chemical Company, New York, material prepared at the Eureka facility and material supplied by FJSRL.

As received, the commercial material from City Chemical Company was light yellow and was caked into a solid mass. Some of this mass was broken up, sieved through a #40 sieve, placed in a glass crystallizing dish and heated in a muffle furnace in a dry room. Gradual increases in temperature up to 250°C failed to produce fusion. Since the reported melting point of $NaAlCl_4$ is 151°C[*], a sample of this commercial material was sent to FJSRL for analysis.

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[*]m.p. 424°K(151°C) - JANAF Thermochemical Tables, 2nd Edition, U.S. Dept. of Commerce, NSRDS-NBS 37, 1971

Investigation at the FJSRL facility, including infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (NMR), x-ray powder diffraction and differential scanning calorimetry (DSC), led to the conclusion that the commercial product was not $NaAlCl_4$, but was principally a mixture of NaCl and $AlCl_3 \cdot 6H_2O$. This material was completely unsuitable for battery use and was not further investigated.

Synthesis of $NaAlCl_4$ at the Eureka facility was carried out as follows: thirty grams of Fisher anhydrous $AlCl_3$ in a large test tube was covered with a layer of fourteen grams of Fisher NaCl. The two layer mixture occupied about one quarter of the volume of the test tube. A rubber stopper fitted with a small glass drying tube containing activated alumina was then plugged into the top of the tube. The tube was immersed into a heating bath at $180^{\circ}C$, up to the level of the interface of the two solids. After about thirty minutes a dark liquid was formed with an undissolved greyish mass at the bottom of the tube. Three days of continued heating caused the greyish mass to reduce to a few undissolved particles at the bottom of the tube. After cooling to room temperature the product was taken into a dry room where the tube was opened and a pea sized piece of aluminum added. The contents were reheated for an additional three days, by which time the aluminum had completely dissolved and the melt was clear and colorless. After cooling, the solid white material was removed from the tube and ground to a fine powder in a glove bag filled with helium. The product was originally very white, but after about thirty minutes exposure to the glove bag atmosphere, some of it had turned a faint yellow. The finished product was labeled $NaAlCl_4$, Batch #1.

A larger scale synthesis was carried out in a 400 ml jar. The procedure was basically the same but this material was never really white. It contained a considerable quantity of dark grey material. When the Al metal was added it did not dissolve but just turned black. When this fused mix was ground, the finished grey powder was labeled $NaAlCl_4$, Batch #2.

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ANOLYTE MIX

Anolyte mixture was prepared from this product. The material was put into a glass crystallizing dish and 10% Cab-O-Sil was mixed in. The mixture was heated to 168°C in a muffle furnace, in a crystallizing dish which was covered with a piece of glass. After sixteen hours, the material was removed from the oven, ground, placed in a glass bottle and labeled Anolyte #2. The fused anolyte was quite easily ground with a mortar and pestle.

A third synthesis of NaAlCl$_4$ was carried out by mixing the AlCl$_3$ and NaCl together and heating this mix in a glass crystallizing dish, covered by a piece of plate glass, in a muffle furnace. This material was heated for one day at 156°C. It did not fuse to produce a solid mass when cooled. Cab-O-Sil was then added and the mix was fused overnight at 168°C. Though this material fused the solidified product crumbled easily when ground. It was placed in a jar and labeled Anolyte #1.

A fourth synthesis of NaAlCl$_4$ was made by mixing AlCl$_3$ and NaCl. The container leaked AlCl$_3$ vapor, and the rubber seals on the oven were destroyed. The material had fused completely, and was labeled NaAlCl$_4$, Batch #4. Cab-O-Sil was then added and a large neoprene stopper inserted into the jar. This mixture fused satisfactorily at 168°C. The product was light grey and was labeled Anoltye #3.

Anolyte #4 was made by mixing 49.7 mole percent AlCl$_3$ with 50.3 mole percent NaCl$_3$ and heating this mix for three days at 168°C. The reaction vessel was a one quart jar capped with a #13 rubber stopper wrapped in Kaiser aluminum foil. The stopper was pushed into the jar and wrapped with vinyl electricians tape to prevent the escape of AlCl$_3$. The vinyl tape was protected by further wrapping with silicone-glass tape. The entire jar and contents were heated in the oven for three days, after which the oven was turned off and the product allowed to cool to room temperature

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in about two hours. The silicone glass tape had deteriorated but no $AlCl_3$ vapor had escaped. The aluminum foil had corroded and the rubber stopper had "hardened". The material in the jar was a relatively clear material which had formed large "needle" crystals upon cooling. There was an opaque, dark grey, mass in the center of the clear material. The jar was then broken and the solid mass that was obtained was broken up with a cast iron mortar and pestle, followed by grinding to powder in a porcelain mortar and pestle.

The opaque material in the center was believed to be uncombined NaCl, so this ground material was reheated for three more days under the same conditions. At the end of the three day period the jar was cooled and the material removed and ground. This time the material was much more transparent. The total weight of the above prepared $NaAlCl_4$ was about 15 ounces.

Enough Cab-O-Sil was added to give a 10% Cab-O-Sil Anolyte. Since the Cab-O-Sil did not disperse uniformly, the entire mix was placed in a one gallon ball mill jar and ball milled for one hour. The anolyte mix was then passed thru a #4 sieve and replaced into the reaction jar as a homogeneous mix. The stopper was covered with new aluminum foil and taped into place. The anolyte mixture was heated overnigh in the oven at $148^\circ C$. A small leak allowed some $AlCl_3$ vapor to escape, causing destruction of the oven gaskets.

Since the Cab-O-Sil renders the anolyte material relatively soft, it was easily removed from the jar and ground to a fine powder. This product was labeled Anolyte #4.

These four anolytes were of sufficient quality and quantity for preliminary testing. The large quanties of anolyte required for extensive single-cell tests and battery construction were provided by FJSRL. Their anolyte material (also containing 10% Cab-O-Sil) was used without modification, except in one case in which Kaolin was mixed to further increase viscosity of the molten anolyte.

CATHOLYTE

A catholyte is a portion of the electrolyte that is specifically associated with the cell cathode and which contains the reactant which undergoes the reduction reaction. The catholyte formula, which was initially supplied by FJSRL had the following composition:

$$40.5 \ ^W/o \ NaAlCl_4 \ 90/10 \ Mix$$
$$45.1 \ ^W/o \ MoCl_5$$
$$14.4 \ ^W/o \ Graphite$$

This specific formula was labeled "Standard Catholyte" to differentiate it from the experimental formulations.

Catholytes #1 and #2 were both standard catholytes made with FJSRL 90/10 mix. These were used in the early single cell testing.

One catholyte formulation contained no carbon, but the results were so poor that this type of catholyte was not further investigated.

Catholytes #3 through #9 were prepared to investigate the effects of the relative amounts of each of the catholyte components. For each of the catholytes #3 through #8, one component was either doubled in concentration or halved in concentration. Catholyte #9 was a standard catholyte used as a control unit for the tests.

Catholyte #10 was the first catholyte made with Eureka fabricated $NaAlCl_4$, and it had a formula similar to a standard catholyte:

$$39.90\% \ Anolyte \ \#1$$
$$44.33\% \ MoCl_5$$
$$15.76\% \ Graphite$$

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Catholyte #11 was the first catholyte used to make batteries. It contained twice the normal concentration of $MoCl_5$ and graphite:

13.5 gm Anolyte #4	25.4 $^w/o$
30.0 gm $MoCl_5$	56.5 $^w/o$
9.6 gm Graphite	18.1 $^w/o$

A factorial design study was performed on the cell data, and as a result of this study another catholyte formulation was chosen:

$NaAlCl_4$ 90/10 Mix	26.12 $^w/o$
$MoCl_5$	58.05 $^w/o$
Graphite	15.83 $^w/o$

This specific formulation was labeled "Battery Catholyte" and was used to make batteries #11 thru #30 (excepting #27).

Battery #27 had cells made with 10 $^w/o$ additional kaolin in the anolyte and 30 $^w/o$ additional kaolin in the catholyte. The kaolin was added to increase the antiflow properties of the electrolytes.

The results of these electrolyte formulations, relative successes or failures, and the relative advantages or problems associated with each electrolyte will be discussed in the appropriate discussion of either the single cell tests or the battery tests.

COSTS

The main ingredient of the fusible electrolyte powders is $NaAlCl_4$. This is prepared from NaCl and anhydrous $AlCl_3$. Cab-O-Sil is added to the $NaAlCl_4$ to make the "90/10 mix". Mallinckrodt, Inc., St. Louis, Missouri quotes;

NaCl, AR crystals(ACS), Code 7581
  4 x 25 lb. case . . . . $0.46/lb.
  100 lb. drum. . . . . $0.27/lb.
  5 x 350 lb. drum. . . . . . . $0.23/lb.

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Fluka Chemical Company quotes:

Anhydrous $AlCl_3$, 0.8% Fe, 79% Cl_2

250 Kilos $4.80/kilo

1000 Kilos. $4.10/kilo

5000 Kilos. $3.60/kilo

Fisher Scientific Company, Chicago, Illinois quotes:

Anhydrous $AlCl_3$, Catalogue #A-574

500 lb. . . . . $105.68/100 lb.

1000 lb. . . . . $104.48/100 lb.

5000 lb. . . . . $103.20/100 lb.

10,000 lb. . . . . $102.98/100 lb.

Mozel Chemical Products Co., St. Louis Missouri quotes:

Cab-O-Sil, EH-5

60 x 10 lb. bags. . . . . . . $1.72/lb.

For as long as the above prices are in effect and for quantities normally purchased for a production battery the cost of the raw materials in an anolyte would be about:

$$
\begin{array}{l}
\text{NaCl} - \$0.104/\text{lb. of anolyte} \\
\text{AlCl}_3 - \$0.839/\text{lb. of anolyte} \\
\underline{\text{Cab-O-Sil} - \$0.172/\text{lb. of anolyte}} \\
\qquad\qquad \$1.115/\text{lb.}
\end{array}
$$

Then a realistic estimate for the price of the raw materials in an anolyte is $1.12 per pound.

A catholyte is just a mixture of anolyte, $MoCl_5$ and graphite.

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Apache Chemical Inc., Seward, Illinois quotes:

$MoCl_5$, particle size -40 +325 (420 microns to 44 microns) with

moisture content as low as possible

Purchases less than 2500 lbs. $11.00/lb.

Purchases between 5000 and

10,000 lbs. $10.00/lb.

Fisher Scientific Co., Chicago, Illinois, quotes graphite, Catalogue
Number G-67:

500 lb. . . . . $115.13/100 lb.

1000 lb. . . . . $111.90/100 lb.

2500 lb. . . . . $109.95/100 lb.

10,000 lb. . . . . $108.62/100 lb.

For as long as the above prices are in effect and for quantities normally
purchased for a production battery the cost of the raw materials in a catholyte
would be about:

Anolyte - $0.291/lb. of Catholyte

$MoCl_5$ - $6.39/lb. of Catholyte

Graphite- $0.174/lb. of Catholyte

$6.86/lb. of Catholyte

Then a realistic estimate for the cost of the raw materials in a catholyte
would be $6.86 per pound.

Lithium-aluminum alloy is an experimental material and it cost $90/lb.
during this program. At this writing no quotes has been received for production
amounts of LiAl alloy.

Two heat sources were used to make these batteries. The $Zr/BaCrO_4$ heat
source is a common production item at Eureka and a good estimate of the cost of
the raw materials in a pound of heat paper is $5.25 per pound.

The Fe/KClO$_4$ is not a common production item at Eureka. However, Pfizer Inc., Metals and Composite Products, New York, New York quotes:

Fe, powdered, NX-1000

500 lb. . . . . $12.85/lb.

1000 lb. . . . . $12.12/lb.

5000 lb. . . . . $11.40/lb.

In 1972 Trona Chemicals, Schiller Park, Illinois quoted KClO$_4$ at about $0.25 per pound for 300 lb. drums.

If these prices remain in effect and for quantities normally purchased for a production battery the cost of the raw materials in the Fe/KClO$_4$ heat source is roughly $9.15 per pound.

In order to get a grasp of the price of the raw materials in an Al/NaAlCl$_4$/MoCl$_5$ battery a comparison will be made with the cost of the raw materials in a production Mg/KCl·LiCl/V$_2$O$_5$ battery manufactured at the Eureka facility. This is a 58 volt, 3.1 amp, 20 second battery that weighs approximately 0.54 pounds and occupies about 5.2 cubic inches of volume. The materials of the production item are here listed and their prices estimated.

Mg/KCl·LiCl/V$_2$O$_5$

INSULATION - THERMAL & ELECTRICAL		$0.74
ELECTRIC MATCH ASSEMBLY		$1.08
CASE AND HEADER		$1.04
CELL CONNECTORS		$0.91
CELL MATERIALS		$1.08
HEAT SOURCE		$0.82
	TOTAL	$5.67

It can be calculated that this battery produces 1.78 whr/lb at a cost of $5.76 which is equal to $3.25/whr.

To estimate the cost of the raw materials in the $Al/NaAlCl_4/MoCl_5$ battery a similar configuration will be considered. Consider a battery which produces 28 volts, 2 amps, with an estimated life of 15 minutes and estimated weight of one pound. There is no reason to believe that anything other than conventional materials will be necessary for this battery so the insulation, match, case, header, and cell connectors will be approximately the same ($3.77). The difference will be the cell materials and the heat source materials. Using the previously estimated costs for the cell materials and considering a battery with fourteen 2.8" diameter cells the cost of the cell materials in one of these $Al/NaAlCl_4$ batteries will be $1.05/battery. The heat source can be estimated at $1.30. This would make the total battery cost (raw materials only) about $6.12. This battery will produce about 14 whr/lb at an estimated $0.44/whr.

A summary of this cost estimate is further illustrated in the following table.

	$Mg/KCl \cdot LiCl/V_2O_5$	$Al/NaAlCl_4/MoCl_5$
INSULATION	$0.74	$0.74
MATCH	$1.08	$1.08
CASE & HEADER	$1.04	$1.04
CELL CONNECTOR	$0.91	$0.91
CELL	$1.08	$1.05
HEAT SOURCE	$0.82	$1.30
	$5.67	$6.12
COST/WHR	$3.24	$0.44

TABLE 1 - ESTIMATED COST OF RAW MATERIALS

SINGLE CELL TESTS

Single cell construction and testing provided the opportunity to gain experience in the processing and handling of the raw materials, as well as a relatively simple means of experimenting with the electrochemical system. The final cell parameters were established on the basis of these tests, and methods of testing and evaluating battery performance were developed from the single cell tests.

The cells were made by compacting dry powders into the form of a three or four layered disk. The top layer was the anode material, the middle layer, the anolyte, and the bottom layer, the catholyte. The fourth layer, when utilized was a layer of nickel dust, which then became the top layer of the cell. The cells were made from the dry, homogeneous, powdered components in the following manner: a 1" diameter circular die was equipped with a tight fitting, but movable, bottom. The bottom layer of the cell, the catholyte, was weighed on an analytical balance and poured into the die. The die was then gently shaken until the surface of the powder was level. Then a tight fitting, but movable, ram was introduced into the die and the level catholyte layer was compacted with a hydraulic laboratory press. The ram was then removed and the middle, anolyte, layer was weighed, poured into the die, leveled and compacted. The remainder of the cell was completed in the same manner. Pressure was then reapplied to the ram until the movable bottom was removed and the completed cell was pushed out of the die. All of the cells tested were made by essentially this procedure. Deviations from this method of cell fabrication will be noted where appropriate.

The purpose of the initial cell tests (#1 through #8) was to develop appropriate test methods and to become familiar with the operation characteristics of this electrochemical system. Subsequent tests (#9 through #19) were performed to

The Cell & Leads are
taped together with
3/16" 3M Glass Tape

The corners of the mica sheets
are taped together with glass
tape to form a nonconducting
shield

Mica

0.004" X 1" Ni
Disc

4 Spot Welds

1" Dia. 3 Layer
Cell

Fiberglass
Sleeve

0.004" X 1" Ni
Disc

0.004" X 1/8"
Ni

Mica

Fiberglass
Sleeve

0.004" X 1/8"
Ni

Single Cell Assembly
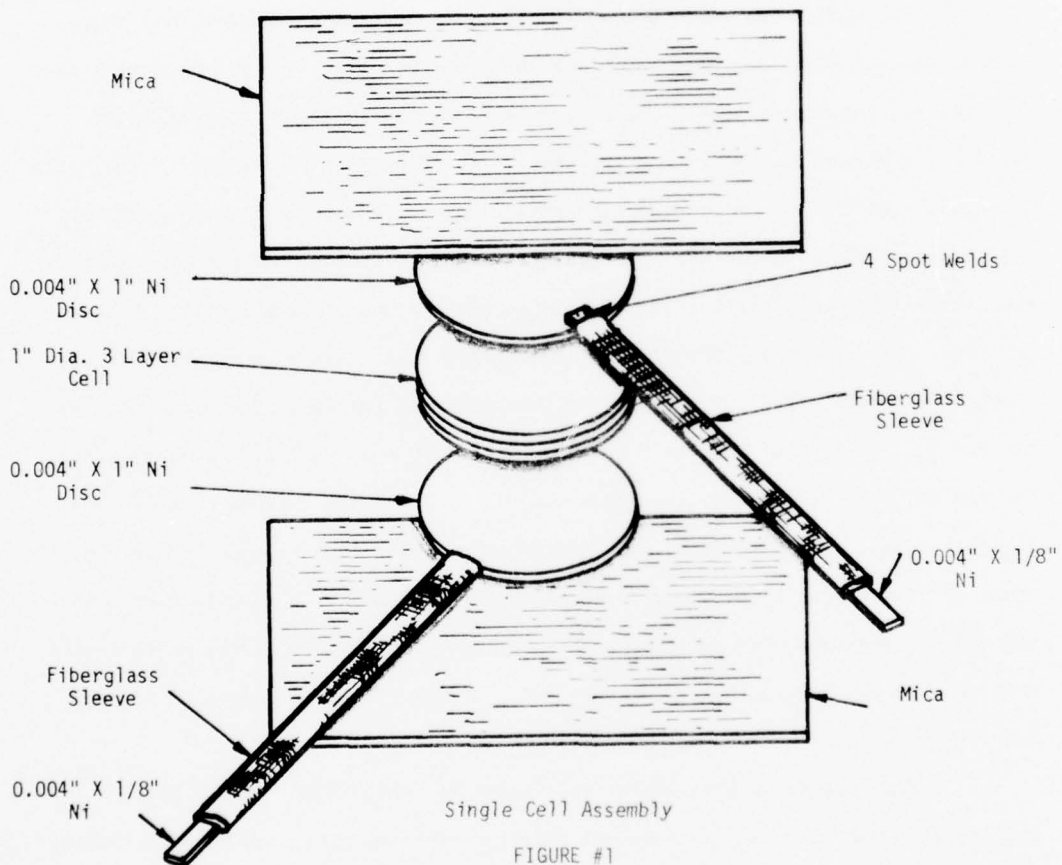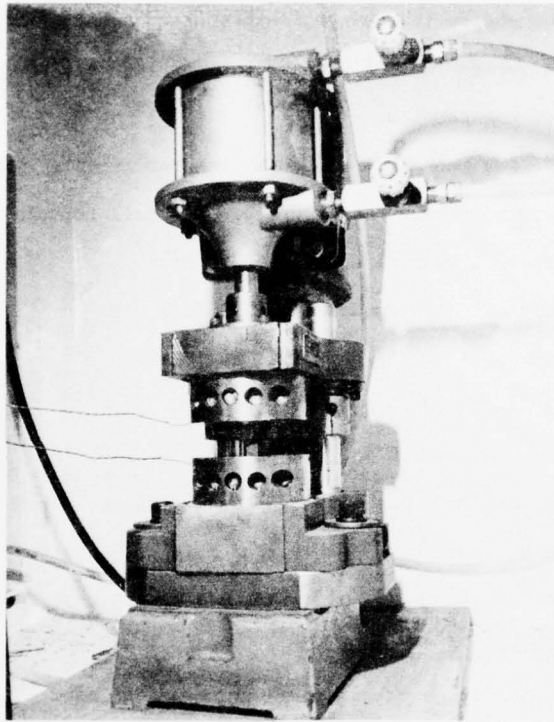
FIGURE #1

FIGURE 2. SINGLE CELL TESTER

observe the effect of variation in composition of the cell components.

The single cell tests proved to be sufficiently reliable and reproducible to serve as criteria for suggesting new cell materials. A factorial design study of the performance of a series of single cells was carried out, and new cells designed on the basis of the results.

Single Cell #1 was made in a one inch diameter circular die with 20,000 PSIG on a Carver Laboratory press. See Figure 1. The cell formula was as follows:

> Anode: 1 gm LiAl alloy (20 ^{W}/o Li)
>
> Anolyte: 0.90 gm NaAlCl$_4$ 90/10 mix
>
> Catholyte: 0.45 gm NaAlCl$_4$ 90/10 mix
>
> 0.50 gm MoCl$_5$
>
> 0.16 gm Graphite

This cell was tested on the old single cell tester. This apparatus consists of two heated, 1" x 3½" dia. platens, spring loaded to keep constant pressure on the cells. The cell was tested with a 25 ohm load and a platen temperature accidentally set at 450°C. A large amount of noxious fumes were evolved, so the test was terminated and the fuming cell quickly removed from the dry room.

Single Cell #2 was constructed in an attempt to reproduce the work done at Seiler. First a catholyte was made up of 4.5 grams NaAlCl$_4$ 90/10 mix, 5.0 grams of MoCl$_5$, and 1.6 grams of graphite. This was shaken together in a one pint jar and called catholyte #1. The cell formula was as follows:

> Anode: 0.375 gm NaAlCl$_4$ 90/10
>
> 0.375 gm LiAl Alloy (20 ^{W}/o Li) |
>
> Anolyte: 0.675 gm NaAlCl$_4$ 90/10   2.25 gm cell
>
> Catholyte: 0.833 gm Catholyte #1

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This cell was tested at $200^{\circ}C$, with a 25 ohm load. No gassing was observed. Single Cell #3 was similar to Single Cell #2, but due to a recorder malfunction only two data points were taken: 1.53 volts at 310 seconds and 0.28 volts at 3500 seconds.

Single Cell #4 had the same cell formula as Single Cell #2. The results were as follows:

V_p = Peak Voltage = 2.07 volts   (Peak Voltage is maximum voltage).

t_{80} = Life to 80% Peak = 3 3/4 min.   (Life is the time from peak to

t_{70} = Life to 70% Peak = 11 1/4 min.   80% or 70% of peak).

R = Load = 25 ohms

To = Initial Temperature = $200^{\circ}C$

I_p = Current at Peak = 0.083 amps

$C.D.$ = Current Density = $0.016 \dfrac{amps}{cm^2}$

R_{INT} = Internal Resistance = Not Measured

The cell area is $0.7854 \ in^2$ or $5.067 \ cm^2$.

Single Cell #5 was a Mg/V_2O_5 control sample. The cell formula was:

  Anode: 0.428 gm of 88% Mg & 12% KCl-LiCl mix

  Anolyte: 0.964 gm 1/3 KCl, 1/3 LiCl, 1/3 Kaolin

  Catholyte: 0.857 gm 1/6 KCl, 1/6 LiCl, 2/3 V_2O_5

This cell was also pressed in the 1" diameter die at 20,000 PSIG and then tested at $450^{\circ}C$. The results follow:

V_p = 2.73 volts To = $450^{\circ}C$

t_{80} = 1 5/8 min. I_p = 0.109 amps

t_{70} = 3 5/8 min. $C.D.$ = $0.0216 \ amps/cm^2$

R = 25 ohms R_{INT} = Not Measured

Single Cell #6 had the same cell formula as Single Cell #2. The load was changed from 25 ohm to 0.66 ohm in order to get a different current density result. The results were:

$$V_p = 0.55 \text{ volts} \qquad To = 200^{\circ}C$$

$$t_{80} = 1/4 \text{ min.} \qquad I_p = 0.83 \text{ amp}$$

$$t_{70} = 1/2 \text{ min.} \qquad C.D. = 0.164 \text{ amp/cm}^2$$

$$R = 0.66 \text{ ohms}$$

Energy densities were determined for each of the remaining cell tests, and are reported over time intervals convering 10% decreases from peak voltage. Voltages were assumed to vary linearly over these ranges, and the mean value of maximum and minimum voltage was taken as the average voltage for the interval.

Since Energy = Power x time, and

$$\text{Power} = iV,$$

$$\text{and } i = \frac{V}{R}$$

then Energy $= \dfrac{V^2 t}{R}$, and

Energy Density $= E/m = \dfrac{\overline{V}^2 t}{mR}$

where $\overline{V}$ = average voltage (for each 10% increment)

t = time (hours)

R = resistance (ohms)

m = mass (pounds)

The internal resistances were measured by momentarily disconnecting the load and observing the change in voltage.

$$R_{INT} = \left(\frac{V_o - V_R}{i_R} \right) X (R)$$

R_{INT} = Internal Resistance
V_o = No-Load Voltage
V_R = Voltage With Load
i_R = Current Thru Load When Voltage Equals V_R
R = Load Resistance

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TABLE 2

SINGLE CELL TEST RESULTS

S.C.#	V_p Volts	t_{80} Sec.	t_{70} Sec.	t_{60} Sec.	t_{50} Sec.	load ohms	T_o °C	I_p amps	C.D. amp/cm^2	E/m whr/lb.	INTERNAL RESISTANCE OHMS at time t seconds	NOTE
7	1.43	105	230	-	-	25	200	0.069	.0137	0.92 Pk to 70%	25.9 at 4200	No Salt in Anode
8	3.25	25	120	180	460	25	200	0.130	.0257	4.34 Pk to 50%	1.5 at 200	Ni Dusted on Anode
9	1.86	-	-	1847	2407	25	200	0.074	.0147	7.97 Pk to 41%	7.05 at 2060	5% $NaAlCl_4$ in Anode
10	1.63	-	700	-	-	25	200	0.065	.0129	3.00 Pk to 70%	2.3 at 170	10% $NaAlCl_4$ in Anode
11	1.63	-	-	1160	-	25	200	0.065	.0129	5.01 Pk to 70%	7.51 at 300	15% $NaAlCl_4$ in Anode
12	1.87	325	1210	-	-	25	200	0.075	.0148	4.52 Pk to 70%	1.16 at 120	20% $NaAlCl_4$ in Anode
13	3.05	50	320	650	1325	25	200	0.122	.0241	11.14 Pk to 50%	1.94 at 60	25% $NaAlCl_4$ in Anode
14	3.07	55	105	250	550	25	200	0.123	.0242	4.81 Pk to 51%	2.0 at 300	20% Smaller Anode
15	2.77	88	243	583	1763	25	200	0.111	.0219	11.30 Pk to 50%	2.5 at 330	10% Smaller Anode
16	2.87	40	140	365	935	25	200	0.115	.0229	6.55 Pk to 51%	1.78 at 500	50% Smaller Anode
17	2.67	61	140	507	2067	25	200	0.107	.0211	11.48 Pk to 52%	1.90 at 300	66% Smaller Anode
18	1.76	5	7	-	-	25	200	0.070	.0139	0.36 Pk to 9.1%	289 at 500	No Graphite
19	2.86	50	210	475	930	25	200	0.114	.0226	6.92 Pk to 50%	3.72 at 1100	Ni on Cathode
20	2.96	47	150	405	1075	25	200	0.119	.0235	7.68 Pk to 50%	1.60 at 530	To Test Anolyte #1
21	3.04	52	84	355	990	25	200	0.122	.0240	7.57 Pk to 50%	4.02 at 1335	To Test Anolyte #2
22	3.06	53	147	733	1913	25	200	0.122	.0242	13.5 Pk to 50%	2.08 at 800	Anode Cut 1/2
23	3.17	52	137	610	1485	25	200	0.127	.0250	12.5 Pk to 50%	2.11 at 640	Anode .275 Cath. 1.305
24	2.80	131	399	822	1967	25	200	0.112	.0221	13.7 Pk to 50%	3.44 at 850	Anode .275 Cath. 1.000
25	2.30	153	266	614	2212	25	200	0.092	.0182	9.67 Pk to 50%	5.99 at 664	Anode .275 Cath. .500
26	3.01	59	233	439	1440	25	200	0.120	.0238	10.8 Pk to 50%	----------	To Test 28% LiAl alloy
27	2.68	98	329	710	2434	25	200	0.107	.0212	14.3 Pk to 50%	----------	Similar to #24 to test 28% LiAl

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TABLE 2 (Con't)

S.C.#	V_p	t_{80}	t_{70}	t_{60}	t_{50}	load	T_o	I_p	C.D.	E/m	INTERNAL RESISTANCE	NOTE
	Volts	Sec.	Sec.	Sec.	Sec.	ohms	°C	amps	amp/cm^2	$whr/lb.$	OHMS at time t seconds	
28	1.00	53	94	135	178	25	200	0.040	.0079	0.22 Pk to 50%	Very High	Recovered to 1.74 with No Load after 180 sec.
29	2.85	55	390	1411	2896	25	200	0.114	.0225	20.6 Pk to 50%	Not Measured	LiAl Dark Colored (28%)
30	2.40	319	526	1057	2710	25	200	.096	.0189	16.2 Pk to 50%	Not Measured	Std. to Test Anol.#3
31	2.55	163	337	667	2618	25	200	.102	.0201	13.9 Pk to 50%	3.0 at 2700	Retest of #30
32	2.46	325	862	2152	3731	25	200	.098	.0193	21.5 Pk to 50%	-	Similar to #23 - Anol. #3
33	2.58	117	311	817	3057	25	200	.103	.0204	16.3 Pk to 50%	1.69 at 330	Std. Cell-2xMoCl5
34	2.14	127	397	1609	1869	25	200	.086	.0169	8.65 Pk to 50%	-	Std. Cell - ½ x MoCl5
35	2.33	107	354	1917	2263	25	200	.093	.0184	12.0 Pk to 50%	4.7 at 2300	Std. Cell - 2 x C
36	2.36	81	260	699	2642	25	200	.094	.0186	11.7 Pk to 50%	-	Std. Cell - ½ x C
37	2.31	60	156	1303	1795	25	200	.092	.0182	8.77 Pk to 50%	1.91 at 200	Std. Cell - 2 x NaAlCl4
38	2.51	150	398	1039	2817	25	200	.100	.0198	15.1 Pk to 50%	-	Std. Cell - ½ x NaAlCl4
39	2.37	191	560	2401	4441	25	200	.095	.0187	22.1 Pk to 50%	-	Std. Cell - Std.Cath. #9
40	2.76	102	442	1097	2412	25	200	.110	.0218	16.1 Pk to 50%	-	#23 - 2 x MoCl5
41	2.12	313	680	2880	3890	25	200	.085	.0167	17.0 Pk to 50%	-	#23 - ½ x MoCl5
42	2.64	55	186	1691	3743	25	200	.106	.0208	21.4 Pk to 50%	-	#23 - 2 x C
43	2.64	111	236	656	2514	25	200	.106	.0208	14.0 Pk to 50%	-	#23 - ½ x C
44	2.33	180	390	1437	3377	25	200	.093	.0184	15.7 Pk to 50%	-	#23 - 2 x NaAlCl4
45	2.80	80	354	1514	2834	25	200	.112	.0221	19.4 Pk to 50%	-	#23 - ½ x NaAlCl4
46	2.65	121	360	1765	3835	25	200	.106	.0209	20.7 Pk to 50%	-	#23 - Std. Cath. #9

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TABLE 2 (Con't)

S.C.#	V_p Volts	t_{80} Sec.	t_{70} Sec.	t_{60} Sec.	t_{50} Sec.	load ohms	T_o °C	I_p amps	C.D. amp/cm²	E/m whr/lb.	INTERNAL RESISTANCE OHMS at time t seconds	NOTE
47	2.25	177	424	1754	-	25	200	.090	.0178	9.6 Pk to 60%	-	Same as #42 Cath. only 0.833 gm
48	2.42	152	512	2334	-	25	200	.097	.0191	14.3 Pk to 60%	-	#23 - 2 x C
49	2.36	68	278	565	1260	15	200	.157	.0311	10.5 Pk to 50%	-	1200 # on Studebaker
50	2.69	47	301	833	-	15	200	.179	.0354	8.6 Pk to 60%	1.12 at 320	17400 # on Studebaker
51	2.35	276	695	1385	-	15	200	.157	.0309	17.2 Pk to 60%	1.38 at 720	10% Total Wt. Off
52	3.02	20	55	334	-	15	200	.201	.0397	6.5 Pk to 60%	2.25 at 90	20% Total Wt. Off
53	2.84	36	102	404	-	15	200	.189	.0374	8.3 Pk to 60%	-	30% Total Wt. Off
54	2.62	52	242	487	-	15	200	.176	.0345	10.8 Pk to 60%	-	40% Total Wt. Off
55	2.88	27	107	272	-	15	200	.192	.0379	8.4 Pk to 60%	1.53 at 300	50% Total Wt. Off
56	1.27	147	180	203	-	15	150	.085	.0167	1.3 Pk to 60%	21.5 at 180	Std. Cell at 150°
57	2.22	174	280	476	-	15	174	.148	.0292	5.2 Pk to 60%	-	Std. Cell at 174°
58	2.43	134	328	626	-	15	204	.162	.0320	7.6 Pk to 60%	-	Std. Cell at 204°
59	2.42	159	276	749	-	15	212	.161	.0318	8.6 Pk to 60%	-	Std. Cell at 212°
60	2.47	116	330	716	2167	15	230	.165	.0325	8.6 Pk to 60%, 18.6 Pk to 50%	-	Std. Cell at 230°
61	2.71	66	225	1030	2125	15	230	.181	.0357	13.2 Pk to 60%, 22.3 Pk to 50%	0.87 at 610	To Test Anol. #4
62	2.78	44	165	448	-	15	255	.185	.0366	6.4 Pk to 60%	0.81 at 480	Std. Cell at 255°C
63	1.80	805	1750	2080	-	15	212	.120	.0237	14.3 Pk to 70%	1.04 at 300	Std. Cell-Burned Off
64	1.92	930	1290	-	-	15	212	.128	.0253	14.6 Pk to 70%	1.42 at 300	Battery Cell - Burned Off Peak
65	2.24	500	1040	1520	-	15	218	.149	.0295	18.9 Pk to 60% & 8.4 Pk to 80%	0.73 at 330	Battery Cell - Burned Off Peak

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TABLE 2 (Con't)

S.C.#	V_p Volts	t_{80} Sec.	t_{70} Sec.	t_{60} Sec.	t_{50} Sec.	load ohms	T_o °C	I_p amps	C.D. amp/cm^2	E/m $whr/lb.$	INTERNAL RESISTANCE OHMS at time t seconds	NOTE
66	2.04	630	960	1325	-	15	218	.136	.0258	14.6 Pk to 60% & 8.8 Pk to 80%	-	Battery Cell-Burned Off Peak - Quenched at Peak
67	1.83	920	1225	1780	2740	15	218	.122	.0241	15.9 Pk to 60% & 10.2 Pk to 80%	0.60 at 400	Battery Cell - Peak Burned Off At No Load Until Plateau
68	2.70	300	650	-	-	15	200	.180	.0355	13.3 Pk to 70% & 7.32 Pk to 80%	-	Double 2 layer cell - Peak not burned off
69	3.46	280	424	643	3360 (52%)	15	200	.228	.0076	6.84 Pk to 50% & 1.89 Pk to 80%	1.38 at 480	2 7/16" dia. - 12.08 gm cell
70	2.64	60	-	-	650	15	225	.176	.0347	-	-	Cell From Battery #23
71	2.42	540	-	-	2520	15	200	.161	.0318	-	-	Cell From Battery #23

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Single Cell #7 had the same cell formula as Single Cell #2 but contained no $NaAlCl_4$ in the anode. The results were:

V_p = 1.43 volts

t_{80} = 105 seconds

t_{70} = 230 seconds

R = 25 ohms

To = 200^oC

I_p = 0.0692 amp

C.D. = 0.0137 amp/cm^2

E/m = Energy Density $\left(\dfrac{\text{watt hours}}{\text{pound}}\right)$ = 0.92 whr/lb.

R_{INT} = 26.0 ohms at 70 min.

It was observed that Single Cell #7 did not appear to have good contact with the Ni lead. Also the anolyte layer was uneven.

Single Cell #8 had the same cell formula as Single Cell #2. However, care was made to keep each cell flat and level, and Ni dust was dusted on the anode side to give better contact with the Ni lead. The results of Single Cell #8 follow:

V_p = 3.25 volts

t_{80} = 25 seconds

t_{70} = 120 seconds

R = 25 ohms

To = 200^oC

I_p = 0.13 amp.

C.D. = 0.0257 amp/cm^2

E/m = 4.34 whr/lb.

R_{INT} = 1.5 ohms at 2 minutes

R_{INT} = 2.17 ohms at 8 minutes

Single Cells #9, #10, #11, #12, #13 were constructed like Single Cell #2 except for varying amounts of $NaAlCl_4$ 90/10 in the anode. The amount was varied from 5%, 10%, 15%, 20% and 25% with Single Cell #9 varied the least amount and Single Cell #13 varied the greatest.

Some of the data for Single Cell #11 were lost due to recorder failure. No correlation between the percentage of $NaAlCl_4$ in the anode and performance was found with this series of tests. Single Cell #13 was notable because of the high voltage and short life. Single Cells #9 thru #12 were made in one day and stored overnight in a vacuum oven at $160^{\circ}F$. Single Cell #13 was made the next day and tested immediately. There was also some fuming with Single Cell #13, but none with the other four cells. It is believed that the vacuum oven caused deterioration of some component of Cells #9 thru #12. Due to the noxious, colored fumes which were formed when Single Cell #13 was tested it appears that $MoCl_5$ was the affected ingredient.

A Standard cell was prepared with the following formulation:

Anode $=$ 0.750 gm LiAl Alloy

Anolyte $=$ 0.675 gm $NaAlCl_4$ 90/10 mix

Catholyte $=$ 0.833 gm Catholyte

It was found that dusting the anode surface with a gram of Ni dust gave better electrical contact with the Ni cell lead so this has been done in each case and this procedure should be considered as part of a standard cell.

Single Cells #14, #15, #16 and #17 were made to test the effect of varying the ratio of the anode mass to cell mass. In Cell #14 the mass of the anode was reduced 20% from that of the standard cell and the difference in weight was added to the anolyte.

Single Cell #14

Anode $=$ 0.600 gm LiAl (20%)

Anolyte $=$ 0.825 gm $NaAlCl_4$ 90/10

Catholyte $=$ 0.833 gm Catholyte #1

Single Cell #15 was made with an anode only 10% smaller than a Standard Cell, and the difference in weight was made up in the anolyte.

<u>Single Cell #15</u>

Anode = 0.675 gm LiAl (20%)

Anolyte = 0.750 gm NaAlCl$_4$ 90/10

Catholyte = 0.833 gm Catholyte #1

Single Cell #16 was made with the anode weight cut 50% (0.375 mg) but the anolyte was only 0.350 gm larger. This was an error, and this cell was 0.25 gm too light.

<u>Single Cell #16</u>

Anode = 0.375 mg LiAl (20%)

Anolyte = 1.025 gm NaAlCl$_4$ 90/10

Catholyte = 0.833 gm Catholyte #1

Single Cell #17 was made with the anode weight 66% less than Standard and the difference in weight made up in the anolyte.

<u>Single Cell #17</u>

Anode = 0.255 gm (20%)

Anolyte = 1.170 gm NaAlCl$_4$ 90/10

Catholyte = 0.333 gm Catholyte #1

The results of these four single cells can be found in Table 2. It can be seen that the two best cells were #15 and #17. These each produced twice as many watt hours per pound as the other two. Since these two cells were the extremes of the series no trend can be seen. Cell #14 was 0.3 volts higher than the other three. Cell #15 had the longest t_{80}, t_{70}, t_{60}, but Cell #17 had the largest t_{50}. No conclusions about anode ratio could be made from these tests.

Single Cell #18 was made with no carbon in the catholyte. These results are also shown in Table 2. The voltage was very low and the life time to 70% of peak was 7 seconds. The internal resistance was noted to be 289 ohms at 500 seconds.
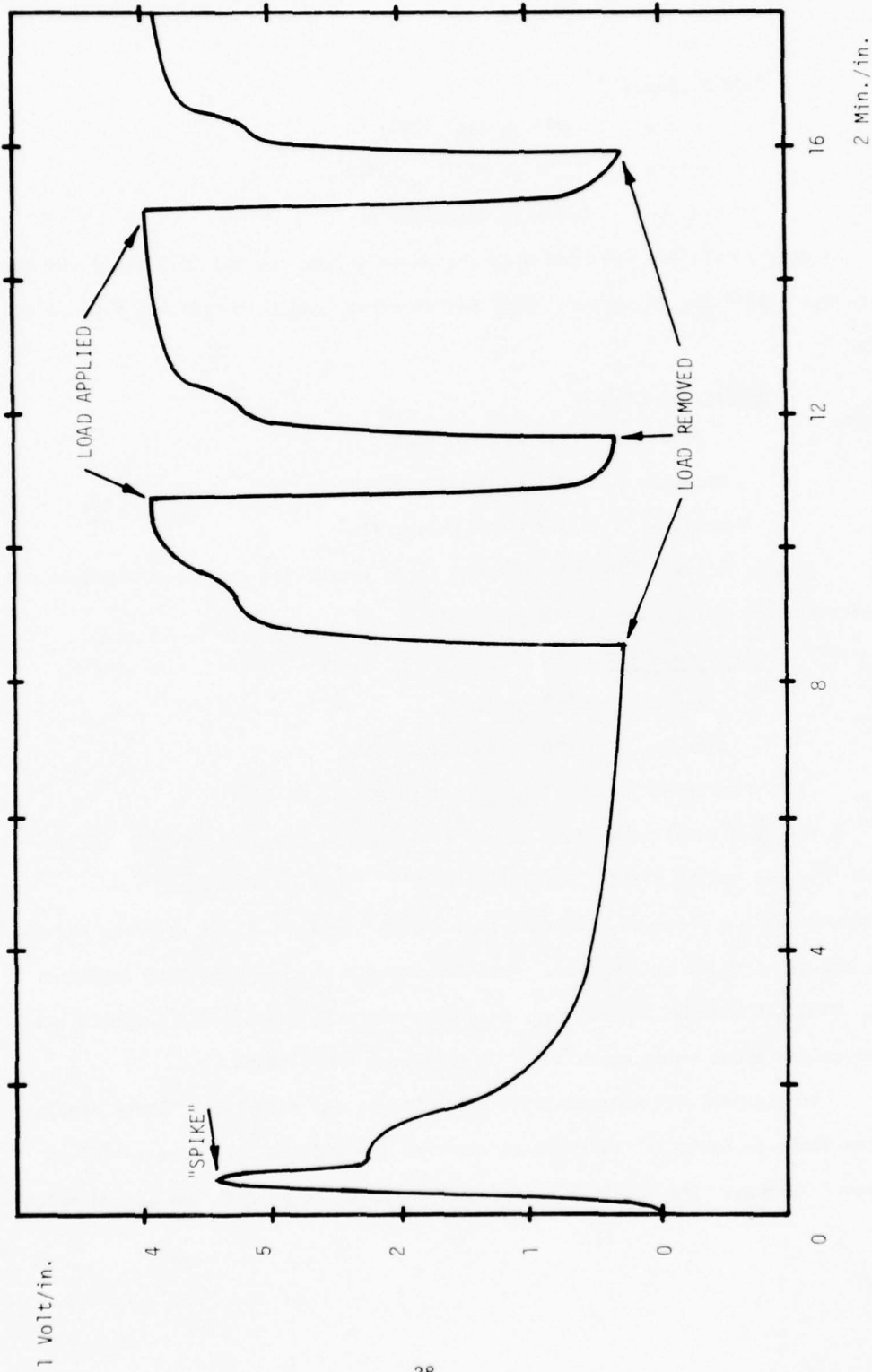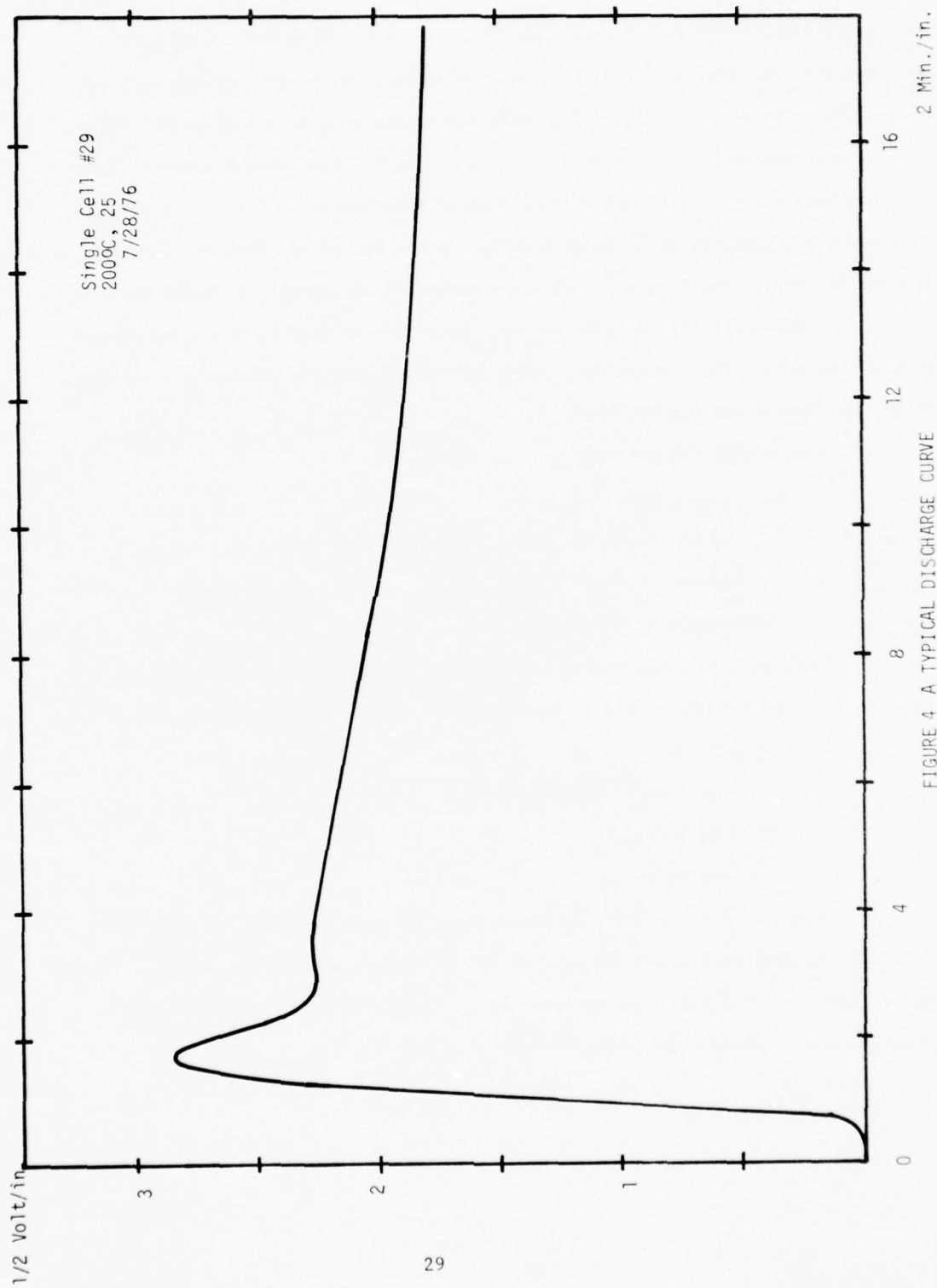
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FIGURE 3. DISCHARGE CURVE OF SINGLE CELL #18

1 Volt/in.

"SPIKE"

LOAD APPLIED

LOAD REMOVED

2 Min./in.

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Single Cell #29
2000C, 25
7/28/76

FIGURE 4 A TYPICAL DISCHARGE CURVE

1/2 Volt/in

2 Min./in.

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An interesting observation was made during the internal resistance measurement. When the load was removed, at 0.16 volts, the voltage recovered exponentially to about 1.68 volts and leveled off for about five seconds to form a plateau. Then the voltage made another exponential rise to 2.0 volts, then formed another plateau. When the load was reapplied the voltage dropped immediately to 0.16 volts again. This cycle was repeated three times and the plateau was always observed in the voltage recovery. See Figure 3. Figure 4 shows a more typical discharge curve.

Single Cell #19 was made to test the effect of dusting Ni on the cathode side of the cell. The results were not very dramatic and the procedure of dusting Ni on the cathode was discontinued.

Single Cell #20 was made to test Anolyte #1.

Single Cell #20

$$\text{Anode} = 0.750 \text{ gm LiAl } (20 \ ^{w}/o \text{ Li})$$

$$\text{Anolyte} = 0.675 \text{ gm Anolyte #1}$$

$$\text{Catholyte} = 0.833 \text{ gm Catholyte #2}$$

The supply of Catholyte #1 was depleted at this point. Catholyte #2 was prepared from the same materials as Catholyte #1, and had the following composition:

Catholyte #2

13.5 gm $NaAlCl_4$ 90/10 (FJSRL)

15.0 gm $MoCl_5$

4.8 gm Graphite

As can be seen in Table 2, the voltage was excellent and the life time and energy density were about the same as the cells made with FJSRL anolyte. Therefore it was concluded that this anolyte was acceptable material and its method of preparation was adequate for this program.

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Single Cell #21 was made to test Anolyte #2. This anolyte was made with Eureka NaAlCl$_4$ and was darker grey than Anolyte #1. It was a standard cell.

Single Cell #21

Anode   =   0.750 gm LiAl (20 ^{W}/o Li)

Anolyte   =   0.675 gm Anolyte #2

Catholyte =   0.833 gm Catholyte #2

The results of this cell test are recorded in Table 2. It can be seen that Anolyte #2 performed almost identically like Anolyte #1. Since it performed so well it was used as the anolyte in the next eight cells.

With the next series of four cells, Single Cells #22, #23, #24 and #25 the mass of the anode was made progressively smaller. It had been noted in the post mortum examination of all of the previously made cells that the anode was not completely consumed. *Cell #22 was made with the anode weight cut 50% and the weight* difference made up in the cathode.

Single Cell #22

Anode   =   0.375 gm LiAl (20 ^{W}/o Li)

Anolyte   =   0.675 gm Anolyte #2

Catholyte =   1.208 gm Catholyte #2

This is similar to what was done with cell series #14 thru #17. In This case, however, the voltage was over three volts and the energy density was higher than any test made up to that time (See Table 2). Single Cell #23 was the next step in the progression.

Single Cell #23

Anode   =   0.275 gm LiAl (20 ^{W}/o Li)

Anolyte   =   0.675 gm Anolyte #2

Catholyte =   1.308 gm Catholyte #2

This cell had the second highest voltage of any cell so far tested. The highest voltage was the 3.25 volts of Single Cell #8, but this cell had an energy density of only 4.34 whr/lb. across the interval from peak voltage to 50% of peak voltage. Single Cell #23 had a voltage of 3.17 volts, but it also had a current density of 25.0 mA/cm^2 and an energy density of 12.5 whr/lb.

Since the anode layer was becoming quite thin it was decided to keep the lower limit at 0.275 gm and begin experimentation on reducing the cathode mass. The difference in cathode weight was made up in an anolyte weight increase.

Single Cell #24

Anode   = 0.275 gm LiAl (20 ^{W}/o Li)

Anolyte = 0.983 gm Anolyte #2

Catholyte = 1.000 gm Catholyte #2

This cell had a voltage slightly lower than the others (2.80 volts) but the energy density was higher than any previously observed, 13.7 whr/lb.

Because Single Cell #24 produced such favorable results, another cell was made with an even smaller cathode and larger anolyte layer.

Single Cell #25

Anode   = 0.275 gm LiAl (20 ^{W}/o Li)

Anolyte = 1.483 gm Anoltye #2

Catholyte = 0.500 gm Catholyte #2

This cell performed well, but the voltage dropped off to 2.30 volts and the energy density to 9.67 whr/lb.

Some conclusions could be made about the configuration of the cell. The anode was too massive. This excess mass absorbed calories but did not produce energy. The anolyte mass to catholyte mass ratio is not at optimum.

At this time a quantity of 28 ^{W}/o LiAl alloy was received at the Eureka facility. To test this new alloy Single Cell #26 was made.

Single Cell #26

        Anode   = 0.750 gm LiAl (28 ^{W}/o Li)

        Anolyte = 0.675 gm Anolyte #2

        Catholyte = 0.833 gm Catholyte #2

As can be seen in Table 2 this was an excellent cell. It had a voltage of 3.01 volts and energy density of 10.8 whr/lb. to 50%. This energy density was higher than that of any other standard cell.

Since the 28 ^{W}/o LiAl alloy made such a good cell another cell was made but with the same cell formula as Single Cell #24.

Single Cell #27

        Anode   = 0.275 gm LiAl (28 ^{W}/o Li)

        Anolyte = 0.983 gm Anolyte #2

        Catholyte = 1.000 gm Catholyte #2

As expected the voltage was lower but the energy density was higher. This cell had a voltage of 2.68 volts and an energy density of 14.3 whr/lb. to 50%.

Single Cell #29 was a repeat of Single Cell #27 except that it was noted that the LiAl alloy (28 ^{W}/o Li) was a darker color due to a few days storage. Nonetheless this cell had a higher voltage than #27, 2.85 volts, and the highest energy density of any cell then tested, 20.6 whr/lb. (See Table 2)

Single Cell #28 was constructed with an anode of pure Al particles. No effort was made to remove the passivation layer from the aluminum. The cell output was poor (Table 2).

Single Cell #28

        Anode   = 0.750 gm Al

        Anolyte = 0.675 gm Anolyte #2

        Catholyte = 0.833 gm Catholyte #2

Single Cells #30, #31, & #32 were made to test the performance of Anolyte #3. Single Cell #30 was a Standard Cell made from Anolyte #3 and Catholyte #2. The anode was LiAl alloy (28 ^{W}/o Li). The peak voltage was 2.40 volts, and the life to 80% of peak voltage was 319 seconds. This was because the usual high voltage peak at the onset of activation was almost absent and the entire discharge curve was flatter. However, the life to 50% was only 2710 seconds, and so the energy density was 16.2 whr/lb.

Single Cell #31 was made similarly to #30. However, in this test the peak voltage was a little higher, 2.55 volts, and the life to 80% was shorter, 163 seconds. The shapes of the bulk of the two discharge curves were almost congruent, but the slightly higher initial peak of Cell #31 was enough to seriously shorten the effective (80%) life. The energy density of Single Cell #31 was 13.9 whr/lb. to 50%.

To this point, Anolyte #3 did not appear to be as good as Anolytes #1 & #2. The voltages for both test cells were lower than expected. Since Single Cell #23 had been a high voltage cell, Anolyte #3 was used to make a cell with configuration similar to #23.

Single Cell #32

Anode   = 0.275 gm LiAl (28 ^{W}/o Li)

Anolyte   = 0.675 gm Anolyte #3

Catholyte = 1.308 gm Catholyte #2

The voltage of cell #32 was similar to that of #30 and #31, 2.46 volts, but the life times were increased, 325 seconds to 80% and 3731 seconds to 50%. This resulted in an energy density of 21.5 whr/lb. to 50%. The long life was caused by two factors. The first factor was that the initial high voltage peak was relatively short and broad. The second factor was that the discharge from this peak to 50% of peak was more linear than for Single Cells #30 or #31. Single Cells #30 & #31 appeared to have a more exponential discharge in the region.

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After testing cells #30, #31, & #32 it could be concluded that lower
voltages could be expected from Anolyte #3. Since approximately a pound of finished
Anolyte #3 remained it was used in the next series of seven single cells and in the
series of seven after that.

Single Cells #33 thru #39 were made to test the formulation of the
catholyte. A "Standard" catholyte has composition as follows:

Component	Wt.	Weight %	Mole %
NaAlCl$_4$ (90/10)	13.5 gm	40.5%	12.2%
MoCl$_5$	15.0 gm	45.1%	10.6%
Graphite	4.8 gm	14.4%	77.2%
Total	33.3 gm	100%	100%

Variations of this standard formula were used to make seven catholytes,
catholytes #3 thru #9.

Catholyte #3 had twice the amount of MoCl$_5$ as the standard catholyte:

13.5 gm NaAlCl$_4$ 90/10 (Anoltye #3)

30.0 gm MoCl$_5$

4.8 gm Graphite (Fisher G-67, Grade #38)

Catholyte #4 had only one half standard quantity of MoCl$_5$:

27.0 gm Anolyte #3

15.0 gm MoCl$_5$

9.6 gm Graphite

Catholyte #5 had twice the standard quantity of graphite:

13.5 gm Anolyte #3

15.0 gm MoCl$_5$

9.6 gm Graphite

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Catholyte #6 had one half standard quantity of graphite:

        13.5 gm Anolyte #3

        15.0 gm $MoCl_5$

         2.4 gm Graphite

Catholyte #7 had twice the standard quantity of anolyte:

        27.0 gm Anolyte #3

        15.0 gm $MoCl_5$

         4.8 gm Graphite

Catholyte #8 had one half the standard quantity of anolyte:

        13.5 Anolyte #3

        30.0 gm $MoCl_5$

         9.6 gm Graphite

Catholyte #9 was the control catholyte and it was made up like a Standard Catholyte:

        13.5 gm Anolyte #3

        15.0 gm $MoCl_5$

         4.8 gm Graphite

A cell was made from each of the catholyte materials. These were Single Cells #33 thru #39. Single Cell #33 was a standard cell made with 28 ^{w}/o LiAl and Catholyte #3. Single Cell #34 was made with Catholyte #4; single cell #35 was made with Catholyte #5, etc. Anolyte #2 was used for all the cells. The results of these cell tests can be found in Table 2.

Single Cell #33 had the highest peak voltage, 2.58 volts, and was followed closely by #38 with 2.51 volts. #34 had the lowest voltage with 2.14 volts. The remaining cells produced voltages grouped around 2.35 volts. #39 had only a modest voltage, 2.37 volts, but had the longest life, 191 seconds to 80% and 4441 seconds to 50% life. This long life gave #39 an energy density of 22.1 whr/lb. to 50%.

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The next best cell was #33 with 16.3 whr/lb. to 50%. #34 was the cell with the lowest voltage.

Some conclusions can be made from this series of tests. The best cell was the standard cell with the standard catholyte. The poorest cell had only one half of the electrochemically active ingredient $MoCl_5$.

A second series of cells was made with these catholytes. This time the cell configuration was like Single Cell #23, the high voltage cell. Single Cell #40 was made with Catholyte #3; #41 was made with Catholyte #4; #42 was made with Catholyte #5; etc. The results of Single Cells #40 thru #46 are given in Table 2.

The higher voltage cells were #45 at 2.80 volts and #40 at 2.76 volts. Then, #42, #43 & #46 had voltages of 2.64, 2.64, and 2.65, respectively. The lowest voltage cell was #41, with 2.12 volts. There were two cells with excellent energy densities, #42 and #46 with 21.4 whr/lb. and 20.7 whr/lb., respectively.

As with the previous series the cell with the standard catholyte was one of the better cells. Also, the cell with only one half the standard quantity of $MoCl_5$ was not very good. But unlike the first series of cells, the one with double $MoCl_5$ was not particularly good, and the one with double graphite was the best in the second series and was not particularly good in the first series. It can be observed that the second series was, as a whole, better than the first series. It is also interesting that #41, with only half the standard $MoCl_5$ had a respectable 80% life. This was because of an unusual, low voltage, double peak at activation. This was also the case with Cell #39, the control cell in series #1. It appears that the effective life to 80% of peak voltage can be increased by leveling the initial high voltage peak. Of course, an even better way to improve the cell would be to broaden this peak. In every case the area after this initial peak was quite linear and desirable for a long life battery.

Single Cell #47 was supposed to be a repeat of #42 but it contained only 0.833 gm catholyte instead of 1.308 gm. Single Cell #48 was a repeat of #42. Note that while the voltage was only 2.42, the life to 60% was 2334 seconds so that an energy density of 14.3 whr/lb. was reached (but to 60% instead of 50%).

A new cell making technique using a Studebaker hydraulic press instead of a Carver laboratory press was tried. Single Cell #49 was made and tested to examine this technique. This cell had the following formula:

$$\text{Anode} = 0.275 \text{ gm LiAl } (28 \text{ }^W/\text{o Li})$$

$$\text{Anolyte} = 0.675 \text{ gm Anoltye } \#1$$

$$\text{Catholyte} = 1.308 \text{ gm Catholyte } \#10$$

Catholyte #10 was made with this formula:

$$\text{Anolyte } \#1 = 39.90 \text{ }^W/\text{o}$$

$$\text{MoCl}_5 = 44.33 \text{ }^W/\text{o}$$

$$\text{Graphite} = 15.76 \text{ }^W/\text{o}$$

The pressure on the Studebaker gauge was 1200 PSIG. The results of the test were as follows:

$$V_p = 2.36 \text{ volts}$$

$$\text{Energy Density} = 10.5 \text{ whr/lb.}$$

$$R_{INT} = 4.29 \text{ ohm}$$

Cell #50 was made with the pressure settings on the press at 14,000 PSIG, 15,200 PSIG, 16,400 PSIG, and 17,400 PSIG, each pressure corresponding to that applied to successive layers of the cell. This cell had a higher voltage and lower internal resistance, 2.69 volts and 1.12 ohms respectively, and it was concluded that this was a suitable technique for making cells.

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A series of five cells, from #51 thru #55, were made and tested with the intent of determining the effect of reducing the overall weight of the cell. Each cell in the series was 10% lighter than the one preceding it.

Single Cell #51:

Anode   = 0.247 gm LiAl (28 ^{W}/o Li)

Anolyte = 0.607 gm Anolyte #1

Catholyte = 1.177 gm Catholyte #10

Single Cell #52:

Anode   = 0.219 gm LiAl (28 ^{W}/o Li)

Anolyte = 0.539 gm Anolyte #1

Catholyte = 1.046 gm Catholyte #10

Single Cell #53:

Anode   = 0.191 gm LiAl (28 ^{W}/o Li)

Anolyte = 0.471 gm Anolyte #1

Catholyte = 0.915 gm Catholyte #10

Single Cell #54:

Anode   = 0.163 gm LiAl (28 ^{W}/o Li)

Anolyte = 0.403 gm Anolyte #1

Catholyte = 0.784 gm Catholyte #10

Single Cell #55:

Anode   = 0.136 gm LiAl (28 ^{W}/o Li)

Anolyte = 0.335 gm Anolyte #1

Catholyte = 0.653 gm Catholyte #10

The results of these tests, Single Cells #51 thru #55, can be found in Table 2. There were no easily recognizable trends through the entire series. For example, the heaviest cell had the lowest voltage and the lightest cell had a high voltage, but not the highest. And the cells in between showed no correlation at all between cell weight and voltage. The heaviest cell did have the greatest

energy density, 17.2 whr/lb. to 60%, but the lightest cell did not have the least. In fact, two other heavier cells produced lower energy densities.

Upon reflecting over past cell series and past Single Cell results it can be seen that the cell outputs are too unpredictable for any real analytical work. By observing the discharge curves it is noticed that the curves are all very similar in the region from 90% to 50%. All of the variability comes from the height and width of the initial high voltage peak.

This initial peak is an unexplained characteristic of this system. It could be caused by the rapid heating of the cell in the Single Cell tester, from the presence of moisture in the cell materials and during the cell testing, from the use of LiAl as an anode material, from impurities in the electrolyte, or from incomplete reaction of the NaCl and $AlCl_3$ to form $NaAlCl_4$. Whatever the cause, this initial peak has been present in almost all of the cells tested so far. Work done at FJSRL indicates that the spike is caused by a surface reaction with the Li in the LiAl anode.

Another series of cells was made to test the effect of temperature on the operation of the cells. These were Single Cells #56 thru #62. Single Cells #56, #57, #58, #59, #60 and #62 all had the same composition.

$$\text{Anode} = 0.750 \text{ gm } 28\% \text{ LiAl Alloy}$$
$$\text{Anolyte} = 0.675 \text{ gm Anolyte } \#1$$
$$\text{Catholyte} = 0.833 \text{ gm Catholyte } \#10$$

Included in, but not a part of, this series was Single Cell #61 which was made to test Anolyte #4.

Single Cell #56 was tested at 150°C. It had a very low voltage of 1.27 volts and very poor energy density of 1.3 whr/lb. to 60%. This was because of an internal resistance of 21.5 ohms at 180 seconds. Single Cell #57 was tested at 174°C and was a volt higher, 2.22 volts, with an energy density of 5.2 whr/lb. to 60%.

Single Cell #58, at 204°C, had an even higher voltage of 2.43 volts and energy density of 7.6 whr/lb. to 60%. Single Cell #59 was tested at 212°C and had a voltage of 2.42 volts and an energy density of 8.6 whr/lb. to 60%. Single Cell #60 was at 230°C and had a voltage of 2.47 volts and an energy density of 8.6 whr/lb. to 60%. Single Cell #62 was at 255°C and had the highest voltage, 2.78 volts, but had an energy density of 6.4 whr/lb. to 60%.

Single Cell #61, which was to test Anolyte #4 was discharged at 230°C. It had an excellent voltage of 2.71 volts and energy density of 13.2 whr/lb. to 60%. It had an internal resistance of 0.87 ohm at 610 seconds and an energy density of 22.5 whr/lb. to 50%.

The next series of cell tests were run in an attempt to improve the effective life of the cell by removing the initial high voltage peak. As has been previously noted this high voltage peak was tall and narrow and seriously interfered with optimizing the energy density. An attempt was made to "burn off" or consume this peak, then cool off the cell, and, then, to test the cell again.

This procedure was somewhat successful. The cells were brought up to 200°C quickly and the peak voltage was noted. The load was immediately disconnected, the cell removed from the single cell tester and placed between two large metal heat sinks to cool. After the cell was cooled to the touch and 0.0 volts read on the voltmeter the cell was again put in the single cell tester and brought up to temperature.

This was the procedure followed with Single Cell #63. Single Cell #63 was a Standard Cell made with Anolyte #4 and Catholyte #11. Catholyte #11 was made with this formula:

<div align="center">

13.5 gm Anolyte #4

30.0 gm MoCl$_5$

9.6 gm Graphite

</div>

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When the hot cell was removed from the anvil noxious red fumes were forming. These condensed onto a glass plate to a pink solid. Some of this pink material turned blue overnight in the dry room while some of the material remained pink for at least a week. This cell had a voltage of 1.80 volts but the 80% life was 805 seconds. This gave an energy density of 14.3 whr/lb. to 70%.

Single Cell #64 was a "battery cell", that is, it had the configuration chosen for the first battery test. The composition was as follows:

Anode = 0.248 gm LiAl 28%

Anolyte = 0.608 gm Anolyte #4

Catholyte = 1.177 gm Catholyte #11

The same "burn off" procedure used for Single Cell #63 was used with #64. This cell had a slightly higher voltage 1.92 volts but due to a higher internal resistance (1.42 ohms instead of 1.04 ohms) it had about the same energy density of 14.6 whr/lb. to 70%.

Single Cell #65 was a repeat of #64 except that every effort was made to disconnect the load at the exact peak voltage. The output of this cell was 2.24 volts with an energy density of 8.4 whr/lb. to 80% or 18.9 whr/lb. to 60%.

Single Cell #66 was similar to #64, & #65 except that the cell was "burned off" with no load, that is, an open circuit. The cell was removed from the single cell tester when the no load peak voltage (3.63 v) was reached. This cell, when tested, had a voltage of 2.04 volts and energy densities of 8.8 whr/lb. to 80% and 14.6 whr/lb. to 60%.

Single Cell #67 was similar to #64, #65, and #66 except the "burn off" procedure was altered. The cell was connected to no load (except the voltmeter) and when the cell reached no load peak (3.66 volts) it was not disconnected. This peak fell off to 2.5 volts within three minutes. When the cell maintained this voltage for one minute the peak was considered burned off and the cell was then removed from the single cell tester, cooled, and tested. Single Cell #67 had

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a relatively low voltage of 1.83 volts but a respectable energy density of 10.2 whr/lb. to 80% and 15.9 whr/lb. to 60%. The internal resistance was 0.60 ohms at 400 seconds.

A factorial design study was made to determine the optimum cell formula. Four variables were studied and were expressed in terms of effect upon peak voltage and 80% life. That is, an attempt was made to make a linear model of the peak voltage, 80% lifetime, and energy density in terms of four cell variables. This would be a model of the form:

$$y = B_0 + B_1 X_1 + B_2 X_2 + B_3 X_3 + B_4 X_4 + B_5 X_1 X_2 + B_6 X_1 X_3 + B_7 X_1 X_4 + B_8 X_2 X_3 +$$
$$B_9 X_2 X_4 + B_{10} X_3 X_4 + B_{11} X_1 X_2 X_3 + B_{12} X_1 X_2 X_4 + B_{13} X_1 X_3 X_4 + B_{14} X_2 X_3 X_4 +$$
$$B_{15} X_1 X_2 X_3 X_4$$

y = peak voltage, 80% lifetime, or energy density

B_0, B_1, B_2, B_3, etc....= constants, determined by the factorial design experiment

X_1, X_2, X_3, X_4 = the four cell parameters under study

After having chosen the three cell characteristics to be studied, it was necessary to choose the four battery parameters to be studied. Four parameters were chosen because a study of five would have required 75 single cell tests. This was considered too lengthy, so a four parameter study with 48 single cell tests was chosen. Since variation in weights of the three cell layers would consume three of the four variables, these weights were examined as ratios of anode weight to anolyte weight and of catholyte weight to anolyte weight. With these two ratios as the variables for the factorial study, the weights of all three layers could be varied and still only consume two variables. So, X_1 = ratio of anode weight to anolyte weight and X_2 = ratio of catholyte weight to anolyte weight.

The anode was only one material (28 ^{w}/o LiAl alloy), and the anolyte was only one active material 90/10 mix; but the catholyte was a mixture of three materials.

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These five variables were examined by redefining in terms of ratios: The ratio of weight of $MoCl_5$ to $NaAlCl_4$ (90/10), and the ratio of graphite to $NaAlCl_4$ (90/10).

X_3 = ratio of $MoCl_5$ weight to $NaAlCl_4$ (90/10) weight

X_4 = ratio of graphite weight to $NaAlCl_4$ (90/10) weight

For this study it was decided to choose a high and low extreme for each variable and then make three cells of each possible combination of high and low extremes. The choice of extremes for these variables was made as follows.

Two types of cells, Standard cells and battery cells, have been defined in this project.

The formula for a Standard Cell is:

Anode = 0.750 gm LiAl Alloy (^{W}/o Li not specified)

Anolyte = 0.675 gm $NaAlCl_4$ (90/10)

Catholyte = 0.833 gm Catholyte

The formula for a battery cell is:

Anode = 0.248 gm 28 ^{W}/o LiAl Alloy

Anolyte = 0.608 gm $NaAlCl_4$ (90/10)

Catholyte = 1.177 gm Catholyte

There have also been two types of catholyte - the Standard catholyte and the battery catholyte.

The formula for a standard catholyte is:

40.5 ^{W}/o $NaAlCl_4$ (90/10)

45.1 ^{W}/o $MoCl_5$

14.4 ^{W}/o Graphite

The formula for a battery catholyte is:

25.4 ^{W}/o $NaAlCl_4$ (90/10)

56.5 ^{W}/o $MoCl_5$

18.1 ^{W}/o Graphite

The ratio of anode to anolyte in a Standard cell is 1.111 and in a battery cell the anode to anolyte ratio is 0.408. The smallest anode weight which can be handled with the 1" die is about 0.200 grams. If 0.200 grams of alloy is put into a Standard cell instead of 0.750 grams, then the anode to anolyte ratio is 0.296. If the 0.200 grams is put into a battery cell instead of 0.248, then the anode to anolyte ratio is 0.329. It is felt that the anode is not totally consumed and that a realistic maximum weight would be 0.500 grams. If 0.500 grams of alloy is substituted for 0.750 grams in the Standard cell, the anode to anolyte ratio becomes 0.741, and the same substitution in a battery cell would produce an anode to anolyte ratio of 0.822. This array of ratios is tabulated below.

$$\text{ratio} = \frac{\text{anode wt.}}{\text{anolyte wt.}}$$

TABLE 3 RATIO OF ANODE WEIGHT TO ANOLYTE WEIGHT

Std. Cell	Batt.Cell	Std. Cell if anode wt.= 0.200 gm	Batt. Cell if anode wt.= 0.200 gm	Std. Cell if anode wt.= 0.500 gm	Batt. Cell if anode wt.= 0.500 gm
1.111 (Hi Extreme)	0.408	0.296 (Lo Extreme)	0.329	0.741	0.822

Catholyte weights of 0.75 grams and 1.3 grams were chosen as reasonable extreme for these weights. A similar table of cathode to anode ratios can be constructed.

$$\text{ratio} = \frac{\text{catholyte wt.}}{\text{anolyte wt.}}$$

TABLE 4 RATIO OF CATHOLYTE WEIGHT TO ANOLYTE WEIGHT

Std. Cell	Batt.Cell	Std.Cell if cath.wt.= 0.75 gm	Batt.Cell if cath.wt.= 0.75 gm	Std. Cell if cath.wt.= 1.30 gm	Batt. Cell if cath.wt.= 1.30 gm
1.234	1.936	1.111 (Lo Extreme)	1.233	1.925	2.138 (Hi Extreme)

Now consider a battery cell with a total weight of 2.25 grams and the extreme Hi anode to anolyte ratio and the extreme Hi catholyte to anolyte ratio.

1) $\dfrac{\text{anode wt.}}{\text{anolyte wt.}} = 1.111$

2) $\dfrac{\text{catholyte wt.}}{\text{anolyte wt.}} = 2.138$

3) anode wt. + anolyte wt. + catholtye wt. = 2.25 gm

Solution of the above three equations gives

anode wt.   =   0.588 gm

anolyte wt.   =   0.530 gm

catholyte wt. =   1.132 gm

Cell formula for

a Hi·Hi cell

Similar calculations yield

A Lo·Lo Cell:

anode wt.   =   0.277 gm

anolyte wt.   =   0.935 gm

catholyte wt. =   1.039 gm

A Hi·Lo Cell:

anode wt.   =   0.776 gm

anolyte wt.   =   0.698 gm

catholyte wt. =   0.776 gm

A Lo·Hi Cell:

anode wt.   =   0.194 gm

anolyte wt.   =   0.655 gm

catholyte wt. =   1.401 gm

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The above four cell formulas yield the four types of cells possible utilizing the two extreme values of the two cell variables chosen for study (anode to anolyte ratio and catholyte to anolyte ratio).

Similar information can be generated for the catholyte. A Standard catholyte is:

$$4.5 \text{ gm NaAlCl}_4 \text{ (90/10)}$$
$$5.0 \text{ gm MoCl}_5$$
$$\underline{1.6 \text{ gm graphite}}$$
$$11.1 \text{ gm total}$$

A battery catholyte is:

$$4.5 \text{ gm NaAlCl}_4 \text{ (90/10)}$$
$$10.0 \text{ gm MoCl}_5$$
$$\underline{3.2 \text{ gm graphite}}$$
$$17.7 \text{ gm total}$$

Good extreme weights are two times the present Standard catholyte weight and one half the present Standard catholyte weight. Then a Hi $MoCl_5$ catholyte would be:

$$4.5 \text{ gm NaAlCl}_4 \text{ (90/10)}$$
$$10.0 \text{ gm MoCl}_5$$
$$1.6 \text{ gm graphite}$$

A Lo $MoCl_5$ catholyte would be:

$$4.5 \text{ gm NaAlCl}_4 \text{ (90/10)}$$
$$2.5 \text{ gm MoCl}_5$$
$$1.6 \text{ gm graphite}$$

A Hi graphite catholyte would be:

     4.5 gm NaAlCl$_4$ (90/10)

     5.0 gm MoCl$_5$

     3.2 gm graphite

A lo graphite catholyte would be:

     4.5 gm NaAlCl$_4$ (90/10)

     5.0 gm MoCl$_5$

     0.8 gm graphite

Then the MoCl$_5$ to NaAlCl$_4$ (90/10) ratios can be calculated and tabulated:

TABLE 5   RATIO OF MoCl$_5$ WEIGHT TO NaAlCl$_4$ WEIGHT

	Hi MoCl$_5$	Lo MoCl$_5$	Hi Graphite	Lo Graphite
$\dfrac{\text{MoCl}_5 \text{ wt.}}{\text{NaAlCl}_4 \text{ (90/10) wt.}}$	2.222 (Hi Extreme)	0.555 (Lo Extreme)	1.111	1.111

The graphite to NaAlCl$_4$ (90/10) ratio can be calculated and tabulated:

TABLE 6   RATIO OF GRAPHITE WEIGHT TO NaAlCl$_4$ WEIGHT

	Hi MoCl$_5$	Lo MoCl$_5$	Hi Graphite	Lo Graphite
$\dfrac{\text{Graphite wt.}}{\text{NaAlCl}_4 \text{ (90/10) wt.}}$	0.247	0.247	0.711 (Hi Extreme)	0.178 (Lo Extreme)

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Now consider the total catholyte weight to be 11.1 gm as in a standard catholyte. Then for a Hi·Hi catholyte:

1) $\dfrac{MoCl_5 \text{ wt.}}{NaAlCl_4 \text{ (90/10) wt.}} = 2.222$

2) $\dfrac{Graphite}{NaAlCl_4 \text{ (90/10) wt.}} = 0.711$

3) $MoCl_5$ wt. + $NaAlCl_4$ (90/10) wt. + Graphite wt. $\approx$ 11.1 gm

Then a Hi·Hi catholyte (that is Hi $MoCl_5$ and Hi graphite) would be:

$NaAlCl_4$ (90/10) = 2.822 gm = 25.43 $^w/o$

$MoCl_5$ = 6.270 gm = 56.50 $^w/o$

C = 2.006 gm = 18.08 $^w/o$

Similar calculations for a Lo·Lo catholyte would yield:

$NaAlCl_4$ (90/10) = 6.405 gm = 57.70 $^w/o$

$MoCl_5$ = 3.555 gm = 32.03 $^w/o$

C = 1.140 gm = 10.27 $^w/o$

A Hi·Lo catholyte would be:

$NaAlCl_4$ (90/10) = 3.265 gm = 29.41 $^w/o$

$MoCl_5$ = 7.254 gm = 65.35 $^w/o$

C = 0.581 gm = 5.24 $^w/o$

A Lo·Hi catholyte would be:

$NaAlCl_4$ (90/10) = 4.898 gm = 44.13 $^w/o$

$MoCl_5$ = 2.719 gm = 24.50 $^w/o$

C = 3.483 gm = 31.38 $^w/o$

Thus the above catholyte formulas represent the four possible catholytes utilizing the four possible combinations of the extreme values of $MoCl_5$ to $NaAlCl_4$ (90/10) ratio and graphite to $NaAlCl_4$ (90/10) ratio.

For each of the four types of cells there would be four catholytes, for a total of 16 different single cells to be made and tested, and if each cell is repeated three times there is a total of 48 single cells to make and test. The sixteen different kinds of cells are each represented by a combination of four symbols. For example, the cell with the high anode ratio (a heavy anode), the low catholyte ratio (a small anode), the low $MoCl_5$ ratio ($MoCl_5$ concentration in catholyte low) and the high graphite ratio (graphite concentration in catholyte high) is represented as HLLH. The entire experiment can be tabulated as:

TABLE 7

SYMBOLS AND CELL NUMBERS

Symbol	Cell Number
HHHH	1 - 17 - 33
HHHL	2 - 18 - 34
HHLH	3 - 19 - 35
HHLL	4 - 20 - 36
HLHH	5 - 21 - 37
HLHL	6 - 22 - 38
HLLH	7 - 23 - 39
HLLL	8 - 24 - 40
LHHH	9 - 25 - 41
LHHL	10 - 26 - 42
LHLH	11 - 27 - 43
LHLL	12 - 28 - 44
LLHH	13 - 29 - 45
LLHL	14 - 30 - 46
LLLH	15 - 31 - 47
LLLL	16 - 32 - 48

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The results of this experiment are tabulated in Table 8.

There were significant qualitative observations as well as quantitative results. For example, there was observed a characteristic high voltage peak for each type of cell tested. These peak shapes are illustrated in Table 8.

Consider Cells #2, #18 and #34 in Table 8. This is a series of cells of type HH with catholyte type HL, and hence designated HHHL. Figure 5 is a reproduction of the data from the first four or five minutes of the three tests. The scale is approximately $\frac{1}{2}$ volt/inch vertically and $\frac{1}{2}$ inch/minute horizontally. A significant feature is the close repeatability of the shape of the peak section of the curve. Figure 6 is a reproduction of the curves for Cells #5, #21 and #37 and is a somewhat more complex shape. Figure 7 is a reproduction of Cells #9, #25 and #41. This peak was most similar to the "spike" experienced on previous single cell tests. Figure 8 is a reproduction of Cells #12, #38 and #44. This figure is included as a representation of the poorest example of reproducible peak shape. All of the other shapes on Table 8 were a better representation than Cells #12, #28 and #44. This observation is significant because what was before considered a random phenomenon now appears to be dependent on the configuration of the four cell parameters studied.

Another qualitative observation is that some cells, regardless of their performance, are too difficult to make to be practical. For example, any cell with a Lo·Hi catholyte is difficult to make because the high concentration of graphite causes the catholyte to crumble easily. Also, any cell with a Hi·Hi designation was hard to make because the anolyte layer was so relatively small that an anolyte layer of uniform thickness could not be produced without "holes" which would allow direct contact of anode and catholyte. Also, a Lo·Hi cell was difficult to prepare because the 0.194 gms of LiAl was such a thin layer that it could not be distributed evenly. In the case of test designation LHLH, eleven cells were attempted to be made

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FACTORIAL DESIGN RESULTS

TABLE 8

| CELL TYPE	CELL #	V_p	T_{80}	ENERGY DENSITY	PEAK SHAPE
HHHH	1	2.43	483	8.62	
	17	2.43	516	9.21	
	33	2.44	504	9.07	
HHHL	2	2.38	556	9.52	
	18	2.46	429	7.85	
	34	2.44	468	8.43	
HHLH	3	2.34	282	4.67	
	19	2.28	272	4.28	
	35	2.28	350	5.50	
HHLL	4	2.47	191	3.52	
	20	2.43	266	4.75	
	36	2.42	299	5.30	
HLHH	5	2.51	360	6.86	
	21	2.57	321	6.41	
	37	2.63	239	5.00	
HLHL	6	2.58	300	6.04	
	22	2.39	333	5.75	
	38	2.68	207	4.50	
HLLH	7	2.13	161	2.21	
	23	2.30	221	3.54	
	39	2.14	117	1.62	
HLLL	8	2.48	161	2.99	
	24	2.43	205	3.66	
	40	2.48	164	3.05	
LHHH	9	2.85	38	0.93	
	25	2.71	166	3.69	
	41	2.86	80	1.98	
LHHL	10	2.58	390	7.85	
	26	2.63	255	5.33	
	42	2.61	355	7.31	
LHLH	11	2.24	380	5.77	
	27	2.23	315	4.74	
	43	2.18	523	7.52	
LHLL	12	2.38	414	7.09	
	28	2.35	468	7.82	
	44	2.35	499	8.33	
LLHH	13	2.40	545	10.14	
	29	2.43	656	11.62	
	45	2.64	724	15.26	
LLHL	14	2.51	494	9.41	
	30	2.42	665	11.78	
	46	2.37	700	11.09	
LLLH	15	2.20	425	6.22	
	31	2.20	353	5.17	
	47	2.12	462	6.28	
LLLL	16	2.42	329	5.83	
	32	2.36	276	4.65	
	48	2.41	346	6.08	
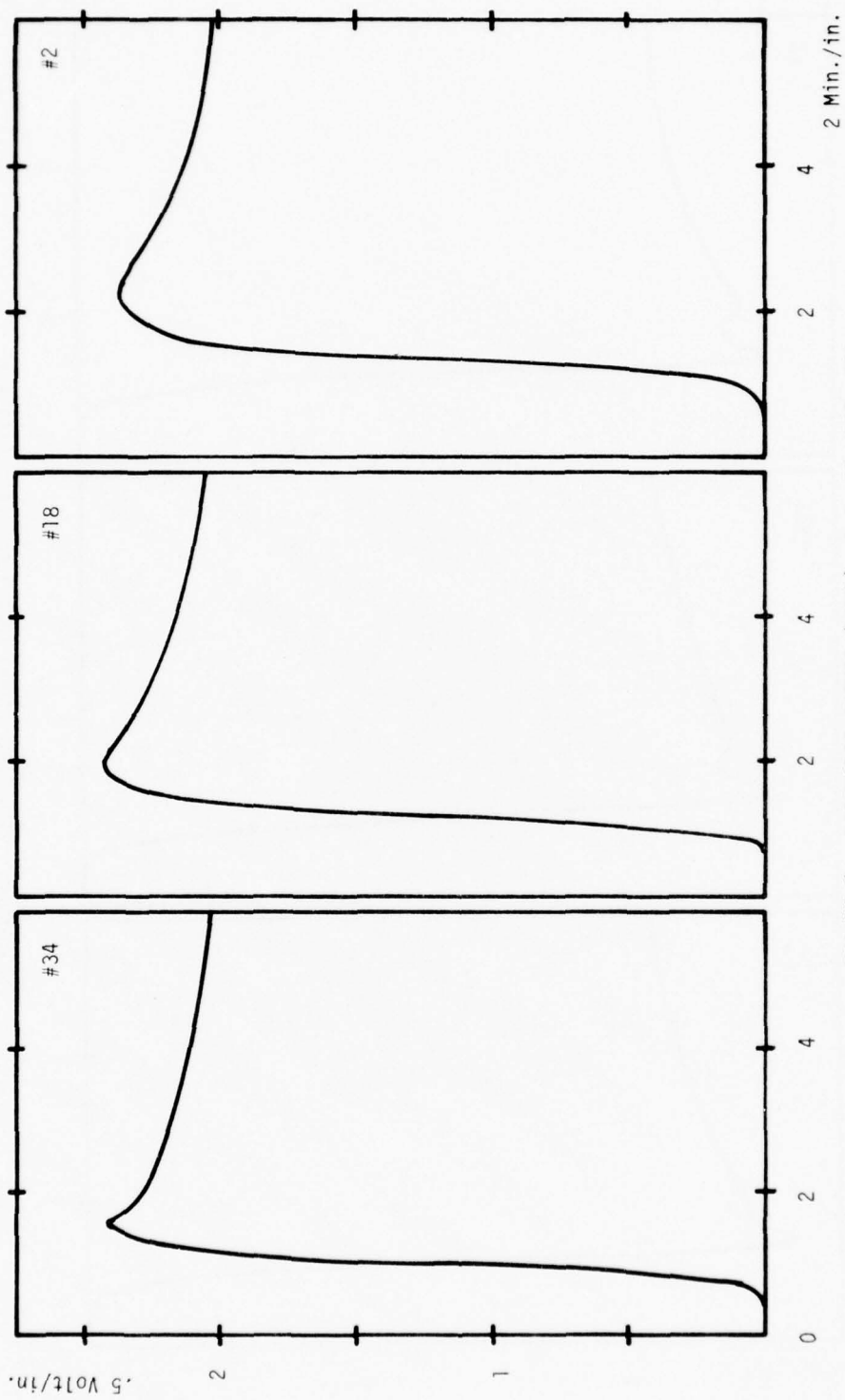
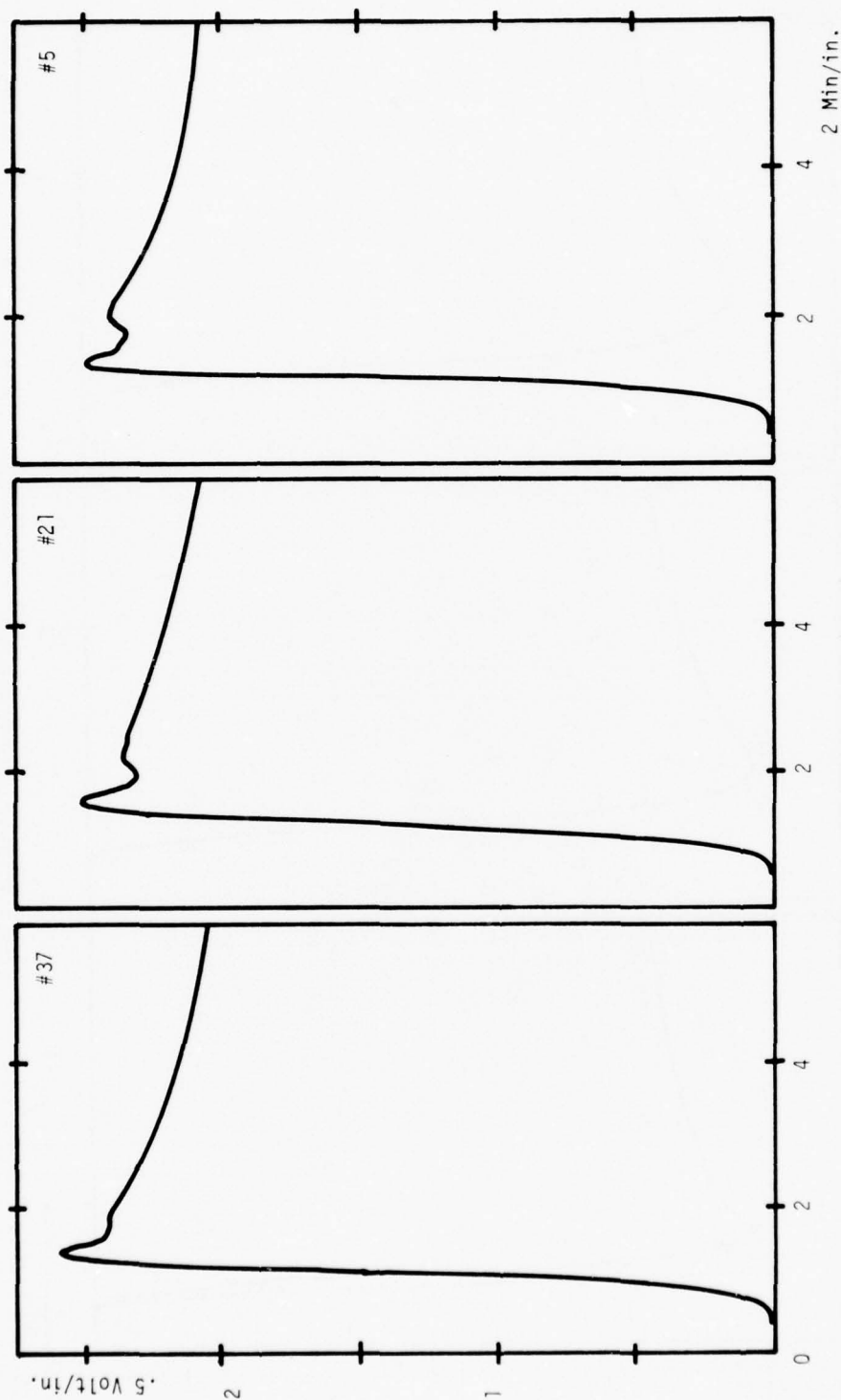FIGURE 5. DISCHARGE CURVES (HHHL) S.C. #2, #18, #34

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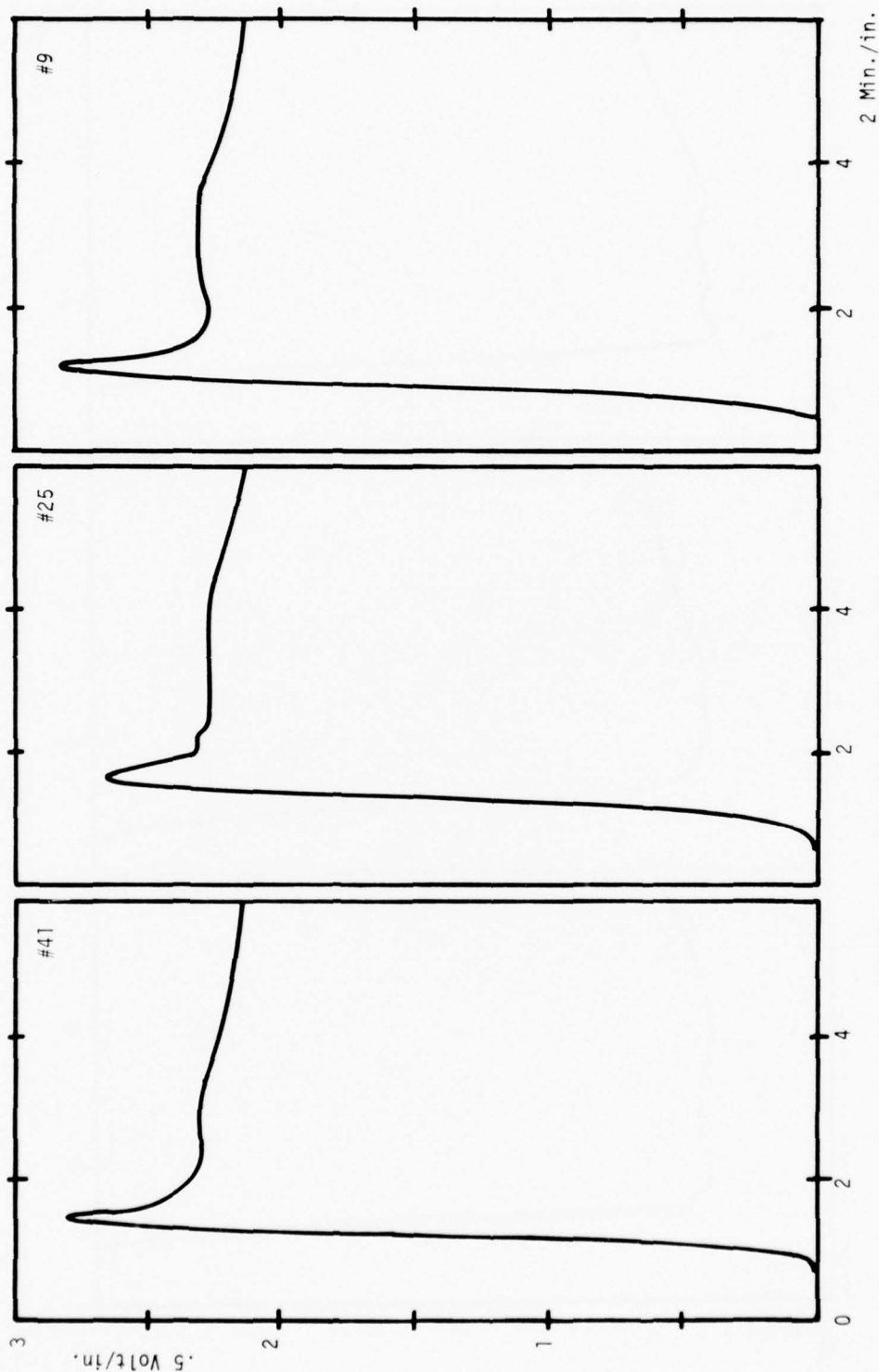FIGURE 6. DISCHARGE CURVES (HLHH) S.C. #5, #21, #37

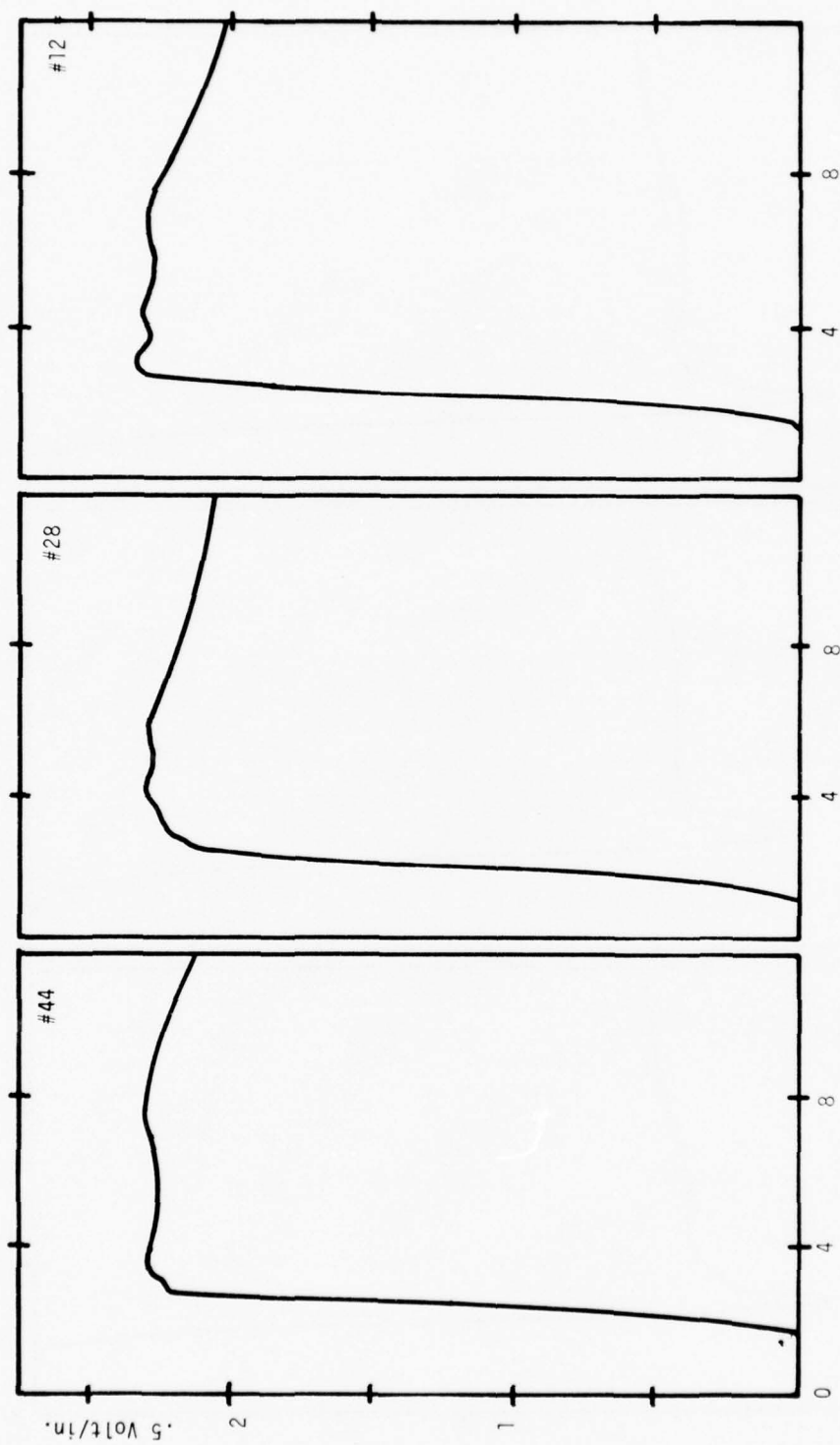FIGURE 7. DISCHARGE CURVES (LHHH) S.C. #9, #25, #41

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FIGURE 8. DISCHARGE CURVES (LHLL), S.C. #12, #28, #44

in order to get three good cells. Six of the cells were of such poor physical quality that they crumbled before they could be assembled into a test unit. Two of the cells tested had much internal shorting and the results were ignored.

The mechanics of processing the data will not be explained here (ref: Introduction to Linear Models and the Design and Analysis of Experiments, Mendenhall, 1968). Two cell characteristics were measured directly, the peak voltage and the 80% lifetime (V_p and T_{80}) and a third characteristic, the energy density, was estimated from these. If the average voltage from peak to 80% peak is considered to be 90% peak then the average current is the average voltage divided by the load resistance.

$$\overline{V} = 0.9\ V_p$$

$$\overline{I} = \frac{0.9\ V_p}{R}$$

Since energy = power x time, and power = voltage x amperage

$$P = \overline{V} \times \overline{I}$$

$$P = (0.9\ V_p)\left(\frac{0.9\ V_p}{R}\right)$$

and

$$E = P \times t$$

$$= \frac{(0.9V_p)^2}{R} \times t$$

$$E = \frac{(0.9V_p)^2 t}{R}$$

Since energy density E/m

$$E.D. = \frac{E}{m} = \frac{(0.9V_p)^2 t}{Rm}$$

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The average voltage is measured in volts, the 80% lifetime was measured in seconds, the resistance was 15 ohms and the cell mass was measured in grams. In order to express the energy density in watthours per pound some conversion factors will need to be added.

$$E.D. = \frac{(0.9V_p)^2}{15 \text{ ohms}} \frac{T_{80}}{60 \cdot 60} \cdot \frac{453.6 \text{ g/lb}}{\text{cell wt. (g)}}$$

Since the cell weight was 2.25 grams

$$E.D. = \frac{(0.9V_p)^2}{15} \cdot \frac{T_{80}}{60 \cdot 60} \cdot \frac{453.6}{2.25}$$

$$E.D. = 0.003024 \ V_p^2 \ T_{80} \ (^{\text{whr}}/\text{lb.})$$

The factorial design experiment generated three linear models, one for peak voltage, one for 80% lifetime and one for energy density estimate.

Peak Voltage:

$$\begin{aligned}
V_p = \ & 2.43 - 0.0085X_1 + 0.0185X_2 + 0.1127X_3 - 0.0298X_4 - 0.0402X_1X_2 - \\
& 0.0394X_1X_3 - 0.01896X_1X_4 + 0.0069X_2X_3 + 0.0198X_2X_4 + 0.0682X_3X_4 - \\
& 0.0502X_1X_2X_3 - 0.00479X_1X_2X_4 - 0.01312X_1X_3X_4 - 0.0069X_2X_3X_4 - \\
& 0.0115X_1X_2X_3X_4
\end{aligned}$$

The sum of the squares of error (SSE) for this experiment was:

$$SSE_{V_p} = 0.1606149$$

Then the variance for the experiment was:

$$s^2 = \frac{SSE}{\text{Deg. of Freedom}} = \frac{0.1606149}{48 - 16}$$

$$= 0.0050192156$$

The standard deviation for the experiment was:

$$S = S^2 = 0.0708464$$

The relative weight of each parameter can be determined by comparing the coefficients of the parameters in the linear model. For example, in the linear model of the peak voltage it is observed that the coefficient of X_1 is - 0.0085 and for X_3 is + 0.1127. Hence it can be said that the variable X_3 (the ratio of $MoCl_5$ to $NaAlCl_4$ 90/10 in the catholyte) is 13 times as important in affecting the peak voltage as X_1 (the ratio of anode to anolyte in the cell). It can also be said that since the coefficient of X_3 is positive, the higher the ratio of $MoCl_5$ to $NaAlCl_4$ 90/10 the higher will be the peak voltage. In like manner it can be said that because the coefficient for X_4 is negative, a high graphite to $NaAlCl_4$ 90/10 ratio will result in a lower voltage.

Another quantitative observation can be made. This linear model was generated from a number of experiments which were averaged together to arrive at one conclusion. This statistical population has a numerical mean and a standard deviation, and hence any single coefficient can be expected to vary when further experiments are performed. What may appear to be important in one experiment could be rather insignificant in the next experiment. Thus, a 99% confidence limit has been chosen. That is, it is assumed that 99% of the experiments performed will give results within 2.576 standard deviations above and below the mean. Any coefficient that is greater than 2.576 standard deviations can thus be assumed to always be significant, and any coefficient less than 2.576 standard deviations could be expected to appear quite high in some experiments, quite low or even negative in others. Therefore, all coefficients less than 2.576 deviations from the mean are ignored as being too undependable to be of significance.

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In the case of the peak voltage, a standard deviation of 0.0708464 was calculated. This number can be used to calculate a 99% confidence band around the mean, which yields the expression:

$$B_{99\%} = B_i \pm 0.02633 \qquad B_i \text{ is the estimate of the co-efficient}$$

$$B_i \text{ (i = 0 thru 15)}$$

$$B_{99\%} = \text{the 99\% confidence band for } B_i$$

The linear model for peak voltage can then be re-examined, and any coefficient that is smaller than this band can be ignored.

$$V_p = 2.43 + 0.1127X_3 - 0.0298X_4 - 0.0402X_1X_2 - 0.0394X_1X_3 + 0.0682X_3X_4 - 0.0502X_1X_2X_3$$

These variables would appear significant in 99 out of 100 experiments.

Similar comments can be made about the 80% lifetime and energy density models.

$$T_{80} = 359.65 - 51.10X_1 - 5.52X_2 + 48.02X_3 - 5.77X_4 + 81.65X_1X_2 + 36.44X_1X_3 + 16.06X_1X_4 - 48.81X_2X_3 - 22.50X_2X_4 - 15.90X_3X_4 + 72.35X_1X_2X_3 + 29.54X_1X_2X_4 + 16.44X_1X_3X_4 - 11.23X_2X_3X_4 + 2.52X_1X_2X_3X_4$$

The sum of the squares for the error is

$$\text{SSE} = 133596$$

The standard deviation is 64.61 and the 99% confidence band is

$$B_{99\%} = B_i \pm 24.02$$

Therefore, the linear model for the 80% lifetime is:

$$T_{80} = 359.65 - 51.10X_1 + 48.02X_3 + 81.65X_1X_2 + 36.44X_1X_3 - 48.81X_2X_3 - 22.60X_2X_4 + 72.35X_1X_2X_3 + 29.54X_1X_2X_4$$

The unreduced linear model for the energy density estimate is

$$E.D. = 6.355 - 0.840X_1 - 0.143X_2 + 1.330X_3 - 0.259X_4 + 1.355X_1X_2$$
$$+ 0.427X_1X_3 - 0.327X_1X_4 - 0.893X_2X_3 - 0.455X_2X_4 - 0.028X_3X_4$$
$$+ 1.193X_1X_2X_3 + 0.552X_1X_2X_4 + 0.216X_1X_3X_4 - 0.325X_2X_3X_4$$
$$+ 0.155X_1X_2X_3X_4$$

The sum of the squares for the error, SSE is

$$SSE = 41.38464945$$

The standard deviation is

$$S = 1.137220425$$

The 99% confidence band is

$$B_{99\%} = B_i \pm 0.4228$$

Thus the significant linear model for energy density estimate is

$$E.D. = 6.36 - 0.84X_1 + 1.33X_3 + 1.36X_1X_2 + 0.43X_1X_3 - 0.89X_2X_3$$
$$- 0.46X_2X_4 + 1.193X_1X_2X_3 + 0.55X_1X_2X_4$$

The variables can now be listed in order of diminishing significance concerning peak voltage:

TABLE 9

PEAK VOLTAGE VARIABLES

$$X_3$$
$$X_3X_4$$
$$-X_1X_2X_3$$
$$-X_1X_2$$
$$-X_1X_3$$
$$-X_4$$

It was observed that the only two significant individual variables were X_3 and X_4, the catholyte variables (the ratio of $MoCl_5$ to $NaAlCl_4$ and the ratio of graphite to $NaAlCl_4$). It is seen that X_3 appears in four of the six factors that are significant to peak voltage, and that the positive coefficients of X_3 and X_3X_4 are greater than the negative coefficients of X_1X_3 and $X_1X_2X_3$. Thus it is concluded that a high ratio of $MoCl_5$ in the catholyte will produce a high voltage cell.

It is also observed that the variables X_1 and X_2 do not prove to be significant individual variables. This implies that the cell formula is not as significant to high voltage as is the catholyte formula. It should be noted that the combinations of high anode weight with high cathode weight and high anode weight with high $MoCl_5$ were detrimental to high voltage. This is demonstrated with variables X_1X_2, X_1X_3, and $X_1X_2X_3$. It should also be noted that the combination of a high $MoCl_5$ ratio and high graphite ratio produces a high voltage cell.

These results must be considered in context with the qualitative observations. Reference to Table 8 shows that the test groups with high $MoCl_5$ ratios or a high combination of $MoCl_5$ and graphite were the tests with the last two digits HH or HL. Of the eight possibilities, six of these had "spike" shaped peaks. If this spike is considered a negative characteristic then the only good cells were HHHH and HHHL, the top two test groups on Table 8. Since the voltage for both of these groups is the same it seems that group HHHH is the most desirable because it produced a high voltage with no trace of a spike.

In order of diminishing significance toward the 80% lifetime, the variables appear as follows:

TABLE 10

LIFETIME VARIABLES

$$X_1 X_2$$
$$X_1 X_2 X_3$$
$$-X_1$$
$$-X_2 X_3$$
$$X_3$$
$$X_1 X_3$$
$$X_1 X_2 X_4$$
$$-X_2 X_4$$

The only two significant individual variables are X_1 and X_3, with X_1 negative and X_3 positive. This means that a large anode can seriously diminish the lifetime of a cell, and a large amount of $MoCl_5$ in a catholyte can significantly increase the life of a cell. More important than anode size considered above is anode size considered as a combination of other variables. This is seen in the two most significant variables, $X_1 X_2$ and $X_1 X_2 X_3$, and to a much smaller degree, $X_1 X_2 X_4$. Note also that five of the eight variables contain X_1 and five contain X_2 while three contain a combination of X_1 and X_2. It can therefore be said that while the cell formula is not too significant in respect to peak voltage, it is certainly significant with respect to lifetime. It should also be noted that of the five significant variables that contain X_1 four of them are positive. This fact can be interpreted as "a long life cell has a large cathode, a small anolyte layer, and a medium sized anode." This interpretation explains the sign and significance of the top three variables in Table 10. Note finally that X_3 appears in four variables, three times as combinations and once as an individual. This can be attributed to the need for a large cathode as well as a large amount of $MoCl_5$ in the catholyte.

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In order of diminishing significance toward the energy density, the variables are as follow:

TABLE 11

ENERGY DENSITY VARIABLES

$$X_1 X_2$$

$$X_3$$

$$X_1 X_2 X_3$$

$$-X_2 X_3$$

$$-X_1$$

$$X_1 X_2 X_4$$

$$-X_2 X_4$$

$$X_1 X_3$$

The most apparent feature is that the factor most significant to high energy density is also most significant to long life. In fact it can be seen that the five most significant factors for energy density are also the five most significant factors for long life. Also, the eight factors that are significant to high energy density are also significant to long life. The only difference is relative order of significance. It can still be said that the best cells have a high anode and cathode weight and a catholyte with a large $MoCl_5$ ratio. These would be the cells designated with HHH for the first three digits. Reference to Table 11 shows that the tests designated HHHH (Cells #1, #17, #33) and HHHL (Cells #2, #18, #34) fit this pattern. It can also be noticed from Table 11 that the test groups LLHH and LLHL had even better energy densities. The only thing these four groups have in common is a large ratio of $MoCl_5$ in the catholyte. This implies that the most significant variable for energy density is ratio of $MoCl_5$ to $NaAlCl_4$ in the catholyte, even though the coefficient of X_3 was smaller than $X_1 X_2$ in the linear model.

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It is also significant that the tests designated LLHH and LLHL had a spike in the peak, but it was relatively small. This caused the energy density to appear better than it actually was, due to the assumption of a linear variation in voltage. In consideration of this, it is concluded that the best cells made were the HHHH and the HHHL.

In summary, the best cell should have a catholyte with a high ratio of $MoCl_5$, a moderate or low ratio of graphite, a moderate or low anode with a moderate or low anolyte layer and a large catholyte layer. These factors should be optimized within the mechanical limits of the fabrication process.

Additional single cells were tested after the factorial design study.

Single Cell #68 was a double two-layer cell. That is, the cell was made of two double layer disks. The top disk contained one layer of catholyte and one layer of anolyte. This was stacked on top of a disk with one layer of LiAl alloy and the bottom layer of nickel dust. In effect this is a four-layer cell with the layers in the following order; catholyte, anolyte, anode, nickel current collector. The anolyte used was Anolyte #4 and the catholyte was Catholyte #11. The cell formulation follows:

<div align="center">

Single Cell #68

Anode   =   0.248 gm LiAl (28 ^{w}/o Li)

Anolyte   =   0.608 gm Anolyte #4

Catholyte   =   1.177 gm Catholyte #11

</div>

This proved to be a good cell. There was only a moderate high voltage spike and the spike was not "burned Off". The peak voltage was 2.7 volts, current density 35.5 mA/cm^2, and the 80% life was 300 seconds. The energy density of the cell was 7.32 whr/lb. to 80% and 13.3 whr/lb. to 70%.

Single Cell #69 was a large diameter battery cell. This cell was 2 7/16" diameter and was made from Catholyte #11 and Anolyte #4. The cell formula for Cell #69 was similar to Cell #68 except that Cell #69 had a total weight of 12.08 gms. Single Cell #69 was tested at 200°C with a 15 ohm load.

Single Cell #69 had the highest voltage (3.46 volts) and the lowest current density (0.0076 amp/cm^2) of any cell tested. The 80% life was 280 seconds and the 52% life was 3360 seconds. The 80% energy density was 1.89 whr/lb and the 52% energy density was 6.84 whr/lb.

Single Cells #70 and #71 were tested to investigate the cells which were used to make Battery #23. Cell #70 was tested at 225°C. This cell had a peak voltage of 2.64 volts and displayed a strong high voltage spike. As a result of this spike, the 80% life was only about 60 seconds and the 50% life was about 650 seconds. Cell #71 was tested at 200°C. This cell had a peak voltage of 2.42 volts with an 80% life of 540 seconds and a 50% life of 2520 seconds. Both cells were tested with a 15 ohm load. The recorder trace for this cell was very similar to that of a HHHH type cell tested in the single cell factorial design study.

The collective data on these cells indicate that the basic design of the cell and the basic catholyte formula are satisfactory.

BATTERIES

For construction of the first batteries it was decided to continue the use of one inch diameter cells used in the single cell tests. The cell formula had been previously tested (Single Cells #64 thru #67), and was as follows:

$$\text{Anode} = 0.248 \text{ gm LiAl Alloy } (28 \text{ }^W/o \text{ Li})$$

$$\text{Anolyte} = 0.608 \text{ gm Anolyte } \#4$$

$$\text{Catholyte} = 1.177 \text{ gm Catholyte } \#11$$

The catholyte was rich in $MoCl_5$ amd graphite. The choice of using five cells was entirely arbitrary.

Heat paper which produced 121 calories/inch^2 was chosen for a heat source. This decision was based on the assumption that the thermal conductivity of the Al/NaAlCl$_4$/MoCl$_5$,C batteries was approximately the same as that of other batteries made by Eureka. Then, if it is assumed that the proper operating temperature of the battery is 200°C, it can be calculated that the proper calorie value of the heat source is about 120 calories/inch^2. Previous experience with heat paper this "cold" has shown that it is usually difficult to handle and does not always burn reliably. However, it was felt that for the first trial of a new, unknown, experimental system the heat paper should be too cold rather than too hot.

When gassing was observed in the single cell testing it was assumed due to vaporization and decomposition of AlCl$_3$ and MoCl$_5$. Thus it was felt that the catholyte could not stand a thermal shock. Therefore, laminated heat paper was used with the hot zirconium/barium chromate mix on one side of the heat pad and the relatively "cold" layer of inert fibers on the other side.

The metal parts of the cell stack (the cell connectors and leads) were made from 0.004" Ni. The positive and negative cell connectors had 4" x 0.093" x 0.004" Ni leads spotwelded to them for welding to the battery header. The cell connectors were shaped like two disks connected by a narrow strip of nickel (dumbell shaped). These were folded over and a heat paper disk inserted to form a finished "heat paper and cell connector subassembly".

The cells were made in the usual manner. The anode, anolyte, and catholyte were weighed in 10 ml. weighing bottles and the cells were pressed, one layer at a time, one on top of the other in a one inch die using the Carver press. This method is slow and tedious but it provides the most reproducible cells. The first batch of seven cells was stored over night in a vacuum oven at 63°C. By morning the cells were so delaminated and deteriorated as to be unusable. A second set of seven cells

were made and these were stored in a desiccator charged with P_2O_5. By morning these cells had also deteriorated and were considered unusable. It was decided to prepare a third set of cells and immediately assemble these into a battery.

Since the cells that had had the high voltage peak burned off gave the highest energy densities, it was decided to apply this treatment to cells that went into construction of the first battery. A procedure was devised so that a cell could be put into the single cell tester, the peak "burned off", the cell cooled down and stored in a P_2O_5 desiccator until all of the cells were so treated. Then the cells were to be used for battery construction. This procedure proved unsuccessful because the burned off cells were physically very hard to handle. They crumbled easily, and the LiAl anode had a tendency to come apart. Also the catholyte had expanded and the cathode was wider than the anode. Also, a large quantity of noxious fumes were released into the room. When this battery was finally assembled and tested, the voltage trace appeared very noisy. This indicates many small localized shorts, probably caused by the thermal deterioration of the cell.

A different procedure was used for the second battery. When the cell connector and heat paper subassemblies were finished they were stacked vertically with freshly built cells in between. Heat paper was inserted in the positive and negative leads and these were placed at the top and bottom of the stack (see Figure 5). The heat paper was always stacked hot side up and the cells were always stacked anode side down. The negative lead was at the bottom of the stack and the positive lead at the top. Two dummy cells were used, one just above the positive lead and one just below the negative lead. Just above the upper dummy cell and just below the lower dummy cell was a heat paper and cell connector subassembly. Beyond these subassemblies were placed 1" dia. pieces of 1/8" thick asbestos. At the top of the stack was placed another heat pad, hot side up, and above this, a 1" diameter mica disk with a 1/4" diameter center hole. At the bottom of the stack were placed
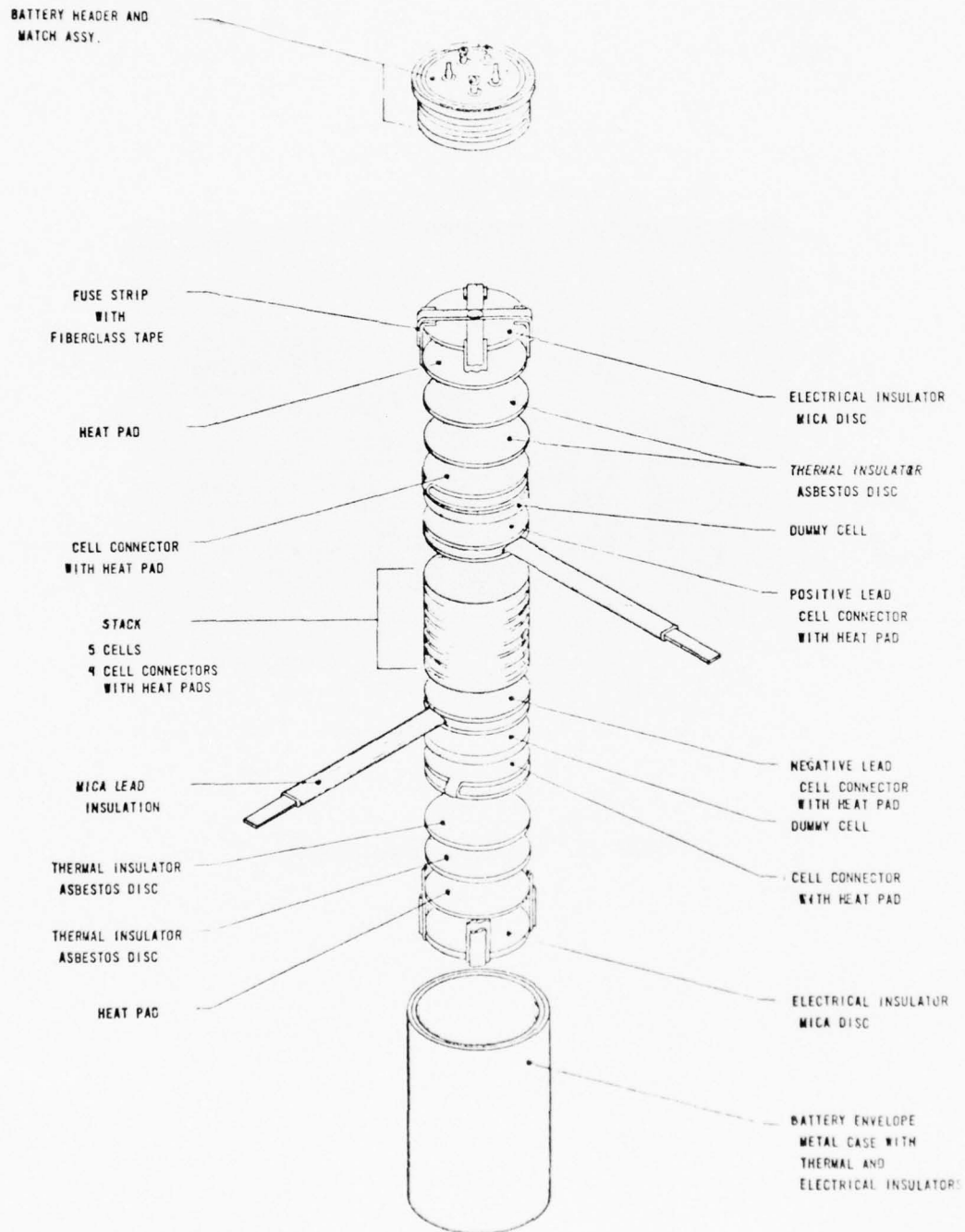
.5 Volt/in.

BATTERY HEADER AND
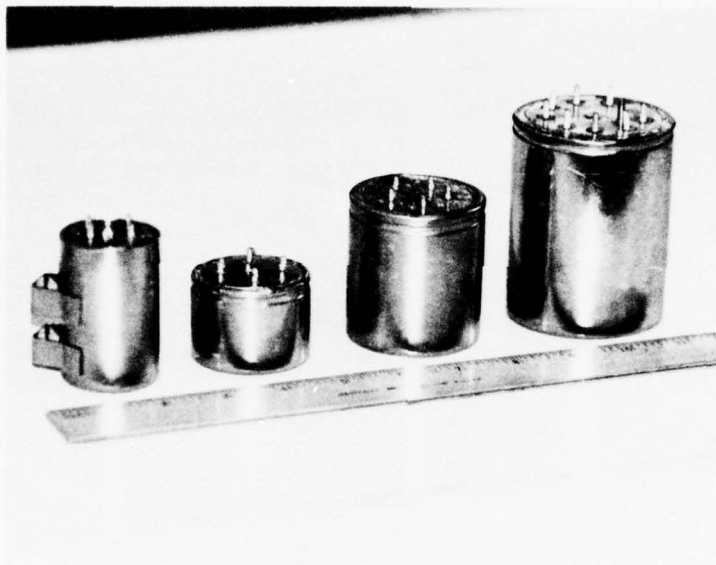MATCH ASSY.

FUSE STRIP
WITH
FIBERGLASS TAPE

HEAT PAD

CELL CONNECTOR
WITH HEAT PAD

STACK

5 CELLS

4 CELL CONNECTORS
WITH HEAT PADS

MICA LEAD
INSULATION

THERMAL INSULATOR
ASBESTOS DISC

THERMAL INSULATOR
ASBESTOS DISC

HEAT PAD

ELECTRICAL INSULATOR
MICA DISC

THERMAL INSULATOR
ASBESTOS DISC

DUMMY CELL

POSITIVE LEAD
CELL CONNECTOR
WITH HEAT PAD

NEGATIVE LEAD
CELL CONNECTOR
WITH HEAT PAD

DUMMY CELL

CELL CONNECTOR
WITH HEAT PAD

ELECTRICAL INSULATOR
MICA DISC

BATTERY ENVELOPE
METAL CASE WITH
THERMAL AND
ELECTRICAL INSULATORS

FIGURE 9. BATTERY CONFIGURATION #1

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FIGURE 10.   A1/C1$_2$ BATTERY DESIGNS

additional asbestos disks followed by another heat pad, hot side up. Finally, at the bottom of the stack was another piece of mica.

The arrangement of five cells, anode down, alternated with four cell connectors is just a standard five cell series stack. The negative lead is, of course, in contact with the anode (28 ^{W}/o LiAl alloy) of the bottom cell and the positive lead is in contact with the catholyte side of the top cell.

The dummy cells serve two purposes. First, they are good heat sinks and since most of the heat is lost at the top and bottom of the stack they tend to store heat upon melting and later return this heat upon refreezing. Also, these cells can be taken out of a fired battery and tested in a single cell tester. Then stack cells can also be taken out of the same fired battery and tested in a single cell tester. A comparison of the data from these two tests should show whether the battery stopped because the electrochemical system was exhausted or because the battery simply cooled off.

The heat pad and cell connector subassemblies on the "outside" of the dummy cells were used in an attempt to provide the continuity of the cell-cell connector alternate pattern. They also helped to maintain the battery temperature.

On the "outside" of the cell connector-heat pad subassemblies were placed asbestos disks. These served to act as thermal insulators and to take up space. This was necessary since the cell stack was much shorter than the can into which the stack was inserted.

On the "outside" of these asbestos disks was placed a heat pad, hot side up, which was to be ignited by the electric match in the header and, in turn, ignite the fuze strips. The fuze strips, in turn, were to burn down the side of the battery and ignite each heat pad in the battery stack. The heat pad at the bottom of the battery was an attempt to compensate, at the bottom of the battery, for the ignition pad and electric match at the top of the battery.

The fuze strips are made by laying two pieces of silicone glass tape on the table top, adhesive side up, in the form of a cross, with each arm of the cross about three inches long. Then a thin 1" diameter mica disk is placed with its center on the center of the cross. Strips of 170 calories/in^2 heat paper, as long as the battery stack is high, are then placed, cold side toward the adhesive, on the tape. Then the entire battery stack is placed on top of the mica disk. Another mica disk, with a center hole, is placed on top of the stack. Now the fuze strips can be lifted up to touch the sides of the stack and are taped across the upper piece of mica. The purpose of the upper piece of mica is to provide a surface to which to tape the fuze strips. The center hole is to allow the electric match in the header assembly to ignite the ignition pad just below the mica disk. The tape from the fuze strips may cover the center hole in the upper mica disk, and then must be cut out with a sharp knife.

The Ni strips on the positive and negative leads are then fitted with silicone glass sleeving and bent upward to be attached to the header assembly.

The stack is now ready to be wrapped with fiberfrax felt until about 1/4" of thermal insulation is built up. The entire assembly is then secured by wrapping with silicone glass tape.

The battery stack is next fitted into the can with additional insulation as necessary. Pads of asbestos can be put in the bottom of the can. All of this padding is primarily to make the battery stack fit snuggly in the can and to provide good thermal insulation.

The positive and negative leads are next spotwelded to two terminals of the header. Two other terminals are used for the electric match. The header is then welded to the battery case and the battery construction is completed.

Since the process of "burning off" the high voltage peak seemed to greatly extend the energy density of the cells, it was decided to "burn off" the cells in battery #1. However, the "burning off" process so deteriorated the cells that the voltage readouts were electrically noisy. The second battery was made of new, fresh cells. When the can was finally welded shut wires were soldered to the positive and negative terminals and connected to a voltmeter. Then the entire battery was placed in an oven at $168^{\circ}C$. After one half hour the battery voltage readout formed a plateau at about 16 volts. When this voltage was maintained for five minutes the battery was removed from the oven and allowed to cool to room temperature overnight, and then subjected to the regular battery test procedure.

The data for the first battery were lost, due to inadvertant reversal of the lead connections. When the battery was fired it appeared to have zero output. When the error was discovered and rectified the voltage had reduced to only 5.3 volts. The activation, peak voltage, and energy density were therefore lost but some useful information was obtained. First, the battery ignited properly, so the heat paper system and the electrolyte system appear to be compatible. Second, the battery did not deform. Therefore, the gasses formed in the system were not enough to be damaging and the battery was certainly not too hot. Third, the readout was noted to be quite "noisy", and hence the "burn off" of individual cells was abandoned in future battery construction.

In the second battery test all data were obtained. The peak voltage was 10.2 volts, or 2.04 volts/cell. This was as high a voltage as any of the "burned off" single cells. The battery produced an amperage of 680 mA and a calculated current density of 134 mA/cm^2. The activation of 0.77 seconds was measured from the time the match fired to the time 80% of the peak was reached. There was also a "cold voltage" of 0.19 volts. The life times of 80%, 70%, 60% and 50% were 65
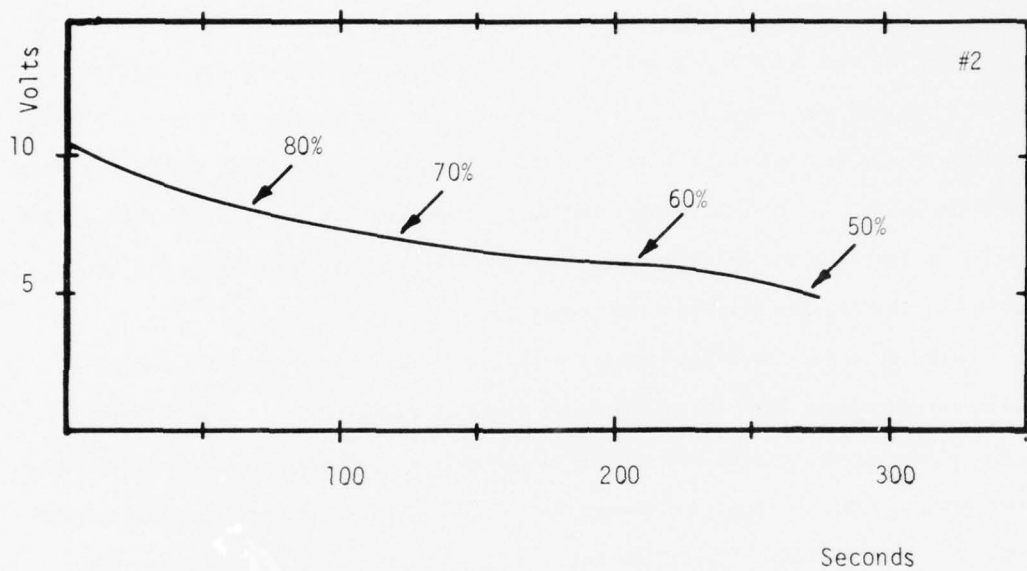
73

FIGURE 11. A_L/C_{L_2} BATTERY DISCHARGE CURVE, (BATTERY #2)

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seconds, 119 seconds, 206 seconds, and 270 seconds, respectively. This yields an energy density of 4.53 whr/lb. to 80% of life, based on the weight of five cells of active material. The energy density for 50% was 12.98 whr/lb.

Battery #3 was made identically to battery #2 except the "burning off" process was not used. The peak voltage of this battery was 11.3 volts or 2.26 volts/cell. The current was 753 mA and the current density 149 mA/cm^2. The activation time to 80% was 1.13 seconds. The 80, 70, 60 and 50% life timers were 42.5, 98, 154, 285 seconds respectively. This yields an energy density of 3.64 whr/lb. to 80% and 13.61 whr/lb. to 50%. The internal resistance was an excellent 0.61 ohms near peak. This gradually increased to 2.9 ohms near the 50% mark. The results are summarized in Table 12.

Battery #4 was made similar to batteries #1, #2, and #3 except that the cells contained a one gram layer of nickel above the anode. The peak voltage of #4 was 10.2 volts. This was the same as battery #2 though the peak was burned off of #2 and not off of #4. Since there were the usual five cells in series this represents 2.04 volts/cell. The current drawn across the 15 ohm load was 680 milliamps and the current density 134 mA/cm^2. This battery had the slowest activation of all batteries produced - 1.66 seconds. This was slower even than battery #10 which was made with cooler heat paper - 115 cal/in^2. The lifetime of battery #4 was 50 seconds to 80% of peak voltage and 325 seconds to 50%. The energy density was estimated at 3.4 whr/lb. to 80% and 19.6 whr/lb. to 50%. This is based on total cell weight of 10.15 grams, and is in reasonably good agreement with data obtained during single cell testing.

From the first four battery tests it was speculated that the calorie value of 121 cal/in^2 was probably too low. So 1" diameter pads of 130 cal/in^2, 140 Cal/in^2, 150 cal/in^2 and 160 cal/in^2 were prepared. The test plan was to make a battery with the 130 cal/in^2 heat paper. If this was good then a battery was to

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TABLE 12

BATTERY TEST RESULTS

Batt. #	V_p Volts	$V/Cell$ Volts/Cell	I_p milli-amps	C.D. mA/cm²	Act. sec.	T_{80} sec.	T_{50} sec.	E/m at 80% whr/lb.	E/m at 50% whr/lb.	$R_{INT.}$ ohms at time t in seconds	NOTES
1	-	-	-	-	-	-	-	-	-	-	Battery Fired-Did Not Vent - Did Not Deform
2	10.2	2.04	680	134	0.77	65	270	4.53	12.0	Not Measured	High Voltage Peak Burned Off Prior To Testing
3	11.3	2.26	753	149	1.13	42.5	285	3.64	13.6	0.61 at 17 0.70 at 55	High Voltage Peak Not Burned Off Prior To Testing
4	10.2	2.04	680	134	1.66	50	325	3.37	19.5	Not Measured	Nickel Layer on Anode
5	11.0	2.20	733	145	-	2.3	17.5	N/A	N/A	Not Measured	Activation Lost - (130 cal./in²)
6	-	-	-	-	-	-	-	-	-	-	Data Lost Due To Technician's Error
7	10.8	2.16	720	142	0.52	51	176	3.99	9.16	Not Measured	Repeat of #5 (130 cal/in²)
8	11.3	2.26	753	149	0.72	35	159	2.97	8.73	Not Measured	Repeat of #5 & #7
9	11.3	2.26	753	149	0.63	31	146	2.65	8.03	6.19 at 204	140 cal/in²
10	11.2	2.24	747	147	1.17	47	245	3.95	12.4	0.58 at 8, 1.21 at 124, 3.83 at 321	115 cal/in²
11	28.8	2.06	1920	379	1.06	10.3	88	2.27	10.8	Not Measured	28 Volt - 14 Cell
12	10.2	2.04	680	134	0.75	86	290	6.31	14.1	0.39 at 110, 1.15 at 298, 0.73 at 240	Room Temp.-Cell Wt.= 1.93 gm, 120 cal/in² Heat Paper
13	11.3	2.26	753	149	1.01	24	223	2.14	11.2	0.94 at 80 1.52 at 210	+165°F - Cell Wt.= 1.94 gm 120 cal/in² Heat Paper

TABLE 12 (Con't)

Batt. #	V_p Volts	$V/Cell$ Volts/Cell	I_p milli-amps	C.D. mA/cm²	Act. sec.	T80 sec.	T50 sec.	E/m at 80% whr/lb.	E/m at 50% whr/lb.	R_INT. ohms at time t in seconds	NOTES
14	4.3	0.86	287	56.6	1.64	138	184	1.81	2.06	6.75 at 120	-65°F - Cell Wt.= 1.939 gm, 120 cal/in² Heat Paper
15	10.8	2.16	720	142	1.57	54	318	3.97	13.8	-	-65°F - Cell Wt.= 2.174 gm, 140 cal/in² Heat Paper
16	10.4	2.08	693	137	1.00	74	285	5.00	12.3	-	+165°F - Cell Wt.= 2.174 gm, 140 cal/in² Heat Paper
17	10.2	2.04	680	134	1.23	36	>420	2.34	>14.9	-	Room Temp.-Thermocouple 115 cal/in²- Cell Wt.=2.179 gm
18	9.4	1.88	627	124	4.35	269	500	14.8	21.7	1.67 at 297 / 4.50 at 572	Sandia Heat Powder- 110 cal/in² 2.183 gm/ Cell-Room Temp. Cell Connectors
19	10.6	2.12	707	139	1.38	153	446	10.9	22.1	1.67 at 105, 1.92 at 227, 4.67 at 378	Repeat of #14-(-65°F) 120 cal/in²
20	10.6	2.12	707	139	1.30	165	325	9.27	15.1	1.69 at 190	Room Temp.-Thermocouple-120 cal/in² - 2.15 gm/cell
21	21.7	1.55	1447	63	2.32	-	-	-	-	-	Double Two Layer Cells Fe/KClO4 Heat Disks No Cell Connector - 14 Large Cells
22	10.0	2.00	667	132	1.23	17	-	-	-	-	Five 1" dia. 3 layer cells Fe/KClO4 Heat Disk with Ni Disk between heat source & catholyte

TABLE 12 (Con't)

Batt. #	V_p Volts	V/Cell Volts/Cell	I_p milli-amps	C.D. mA/cm^2	Act. sec.	T_{80} sec.	T_{50} sec.	E/m at 80% whr/lb.	E/m at 50% whr/lb.	$R_{INT.}$ ohms at time t in seconds	NOTES
23	10.9	2.18	727	143	1.18	14.2	30.0	-	-	-	Fe/KClO4 Heat Disks with Cell Connectors
24	12.7	2.54	847	167	0.32	8	-	-	-	-	Fe/KClO4 Heat Disks with 170 cal/in² fuze strips
25	12.4	2.48	827	163	0.40	49	134	5.13	10.21	2.41 at 150	Fe/KClO4 Heat Disks New Anolyte & Catholyte
26	12.8	2.56	853	168	0.36	7.7	26.1	-	-	-	120 cal/in² heat pads
27	11.6	2.32	773	153	0.63	62.1	126	5.81	8.90	-	30% Kaolin in Catholyte & 10% Kaolin in Anolyte - 120 cal/in2 fuze strips
28	14.5	2.90	290	57.2	0.29	15	397	0.64	9.83	1.5 at 190 / 3.2 at 350	Load - 50 ohms Fe/KClO4 Heat Disks
29	11.4	2.28	228	45.0	0.35	310	900	8.34	15.4	-	Anode = 15% Anolyte = 30% Catholyte = 55%
30	28.2	2.56	806	43.4	< 1 sec.	362	754	10.4	16.7	1.24 at 400	1.914" dia. cell; 11 cells; Fe/KClO4 Heat Disks; 35 Load

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be made of 140 cal/in^2 heat paper, and so on until the battery was obviously too hot. It was felt that 160 cal/in^2 heat paper was surely the extreme high value of heat paper calorie value.

Battery #5 was the first battery of this series and it was made with 130 cal/in^2 heat paper. The battery was otherwise the same as batteries #1, #2, #3 and #4. This battery produced a peak voltage of 11.0 volts, or 2.2 volts/cell, with a current of 733 mA and a current density of 145 mA/cm^2. The activation of this battery was not recorded due to a technician's error. The lifetime of 80% was 2.3 seconds! There was no evidence of internal shorting (electrical noise) in the recorder trace. The 50% life was about 17.5 seconds. These results were quite unexpected, even if the 130 cal/in^2 proved to be too hot. A post mortum examination of the battery showed the cell stack fused together, and the fiberfrax insulation looked as though blue dye had leaked thru it. There was no real evidence that the anolyte had flowed and the catholyte, while it appeared to swell 10%, did not appear to flow either. There appeared to be no hot spots or shorting around the edges of the cell. It was concluded that the battery may have been too hot, but the specific effects of the excess heat were not apparent.

It was decided to test two more batteries, a control unit for the other. Battery #6 was made with 121 cal/in^2 heat paper and #7 was made with 130 cal/in^2 heat paper. All anolytes, catholytes, cell formulas and other parameters were kept the same as for battery #5. The test data for battery #6 were lost due to a technician's error. However, the problem was corrected, and battery #7 was successfully tested. The data from battery #7 were not as good as data for previous batteries but was certainly better than battery #5. The peak voltage was 10.8 volts (2.16 volts/cell). The current at peak was 720 mA and the current density was 142 mA/cm^2. The 80% life was 51 seconds and the 50% life 176 seconds. The energy

density was 4.0 whr/lb. at 80% and 9.16 whr/lb. at 50%, and activation time was 0.62 seconds. The post mortum examination of this battery was almost identical to that of #5 except that the stack was not as difficult to take apart. That is, it had fused together but not as extensively as had #5. It is notable that to a limit of 80% life, this battery had the highest useful energy density of any tested so far, and the activation time was excellent.

A third 130 cal/in^2 battery, #8, was constructed. Battery #8 was a repeat of #7 and #5, which had given very different performance despite their similar construction. The peak voltage of battery #8 was 11.3 volts (2.26 volts/cell). The peak current was 752 mA and the current density 149 mA/cm^2. Activation time was 0.72 seconds. The life time to 80% was 34.7 seconds and the 50% life was 159 seconds. The energy densities were 2.86 whr/lb. to 80% and 8.73 whr/lb. to 50% life. The post mortum examination of #8 was similar to #5 and #7. There was thus provided no explanation of the catastrophic failure of battery #5.

Though not catastrophic failures, the lifetimes of batteries #7 and #8 were shorter than the batteries made with 121 cal/in^2 paper. Presumably a battery made with 140 cal/in^2 would have an even shorter lifetime. This was shown to be the case with battery #9. Battery #9 was the same as batteries #5, #6, #7, and #8 except that it was made with 140 cal/in^2 heat paper. The peak voltage was 11.3 volts (2.26 volt/cell). The peak current was 752 mA and the current density was 149 mA/cm^2. The 80% and 50% lifetimes were 31 seconds and 146 seconds, respectively. The energy density was 2.65 whr/lb. to 80% and 8.03 whr/lb. to 50%. The activation was 0.63 seconds. This battery had the poorest performance of any battery tested except #5. The activation was the quickest. Since this battery followed the "hotter paper, shorter life" trend, no batteries were made from the 150 and 160 cal/in^2 paper.
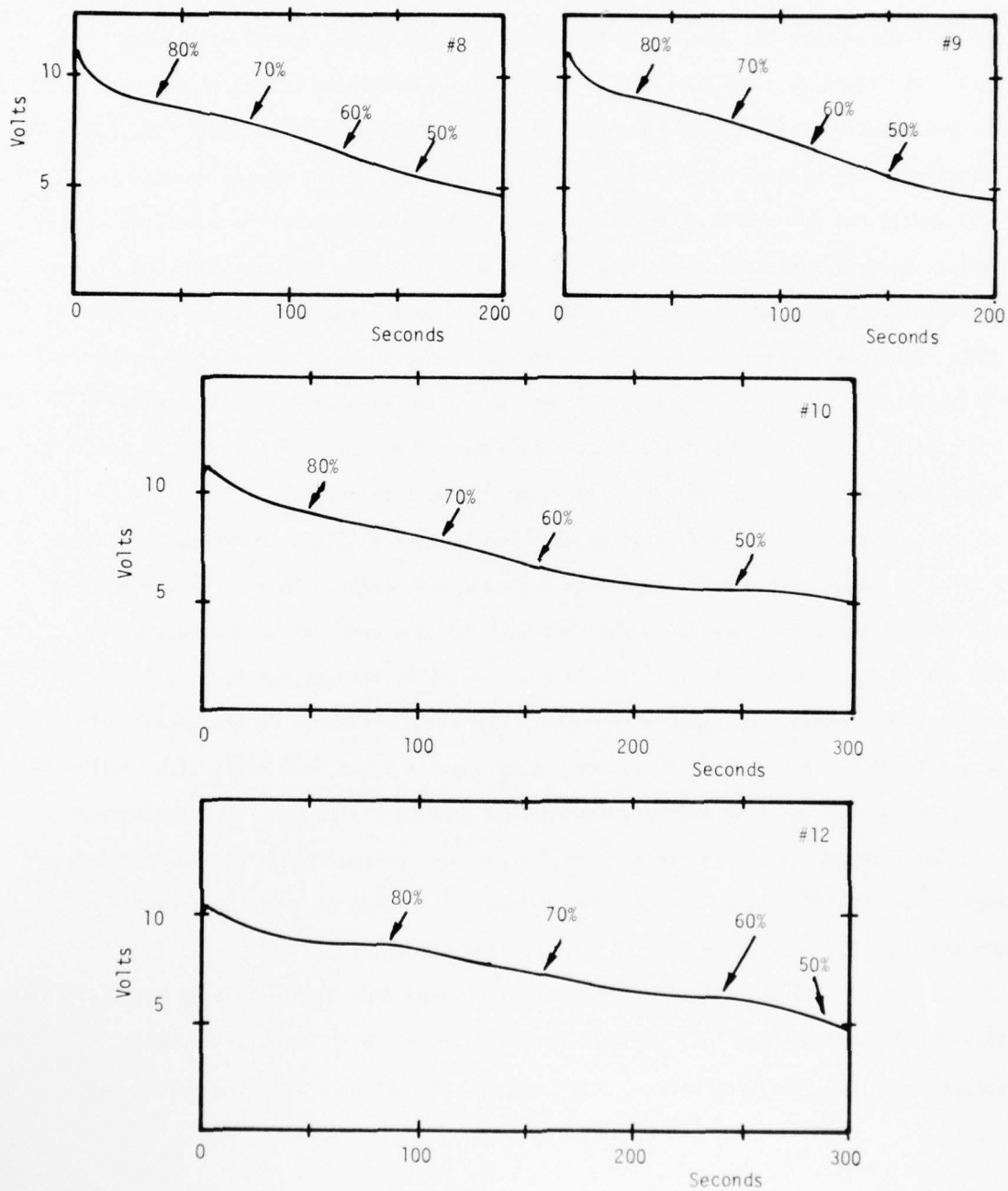
FIGURE 12. A_L/C_{L_2} BATTERY DISCHARGE CURVES (BATTERIES #8, 9, 10, & 12)

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Two new calorie values of heat paper were ordered - 110 cal/in^2 and 115 cal/in^2. Battery #10 was made with 115 cal/in^2 heat paper with the other battery and cell parameters the same as #5 thru #9. Battery #10 had a peak voltage of 11.2 volts (2.24 volt/cell). This battery had a peak current of 747 mA and a current density of 147 mA/cm^2, and the activation time was 1.17 seconds. The 80% lifetime was 47 seconds and the 50% life was 245 seconds. The energy density was 3.95 whr/lb. at 80% and 12.4 whr/lb. to 50%. Internal resistance measurements were made at several intervals. At 8 seconds the internal resistance was 0.58 ohm, at 124 seconds it was 1.21 ohms, and at 321 seconds the internal resistance was 3.83 ohms. This performance was better than the hot batteries but not as good as the 121 cal/in^2 batteries, and so no additional batteries were constructed with the 110 cal/in^2 paper. It was decided that the original estimate of 121 cal/in^2 was a good estimate of the optimum calorie value of the heat paper.

One of the goals of this program was to make a 28 volt battery. Therefore, a battery with fourteen cells in series was made and tested. This battery contained 120 cal/in^2 heat paper and 1.833 gram cells. The same case was used as was used for all of the five cell batteries. This was possible because the five cell batteries contained many asbestos "spacers", which were removed to accommodate the larger 14 cell stack. The peak voltage of this battery was 28.8 volts (2.06 volt/cell). The peak current was 1.92 amps and the current density 379 mA/cm^2. The activation time was 1.06 seconds. The internal resistance was measured at 67 seconds as 2.36 ohms. The lifetime was 10.3 seconds to 80% and 88 seconds to 50%. The energy density was 2.27 whr/lb. at 80% and 10.8 whr/lb. at 50%.

The cells for the first nine batteries were made singly by hand with a 1" diameter die and pressed on a Carver laboratory press. Each layer was weighed individually in a weighing bottle. Then the contents of each weighing bottle were
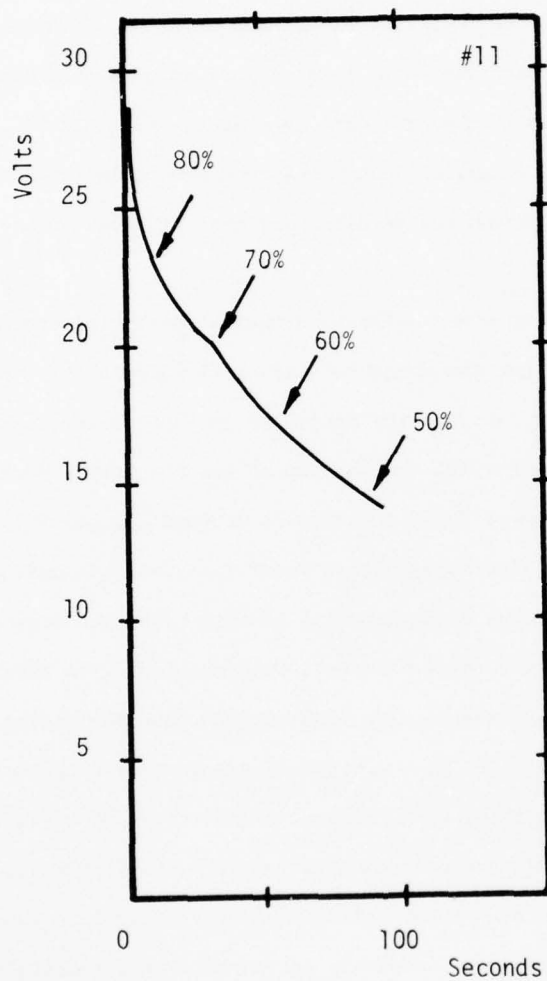
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FIGURE 13. A_L/C_{L_2} BATTERY DISCHARGE CURVE (BATTERY #11.)

poured into the die and compacted, the catholyte first, then the anolyte on top of that and then the anode on top of that. If nickel was used, a fourth layer was compacted on top of that. In all cases the final layer was compacted with a force of 20,000 pounds on the 1" ram. This procedure is relatively repeatable, but it is slow and tedious. It is nearly impossible to construct more than one battery per day using this process, so a search for an alternate cell fabrication method was made.

At the Eureka facility other pelletized thermal batteries are made with hydraulic presses which meter out the amount of each cell material by changing the volume of the die cavity. For example, the bottom of the die cavity can be lowered to about 1/16", filled with catholyte, and the top of the die cavity scraped with a straight edge. Then the bottom of the die cavity is dropped another 1/16", and the anolyte layer added. This is also scraped to a level fill, and the bottom of the cavity is dropped once again. The anode material is then added and scraped level. The ram is next brought down, and the entire cell is compacted. The distance that the bottom of the die cavity is dropped each time depends upon the desired weight of the layer, and must be determined by a process of trial and error. Once the weights have been "set in" (that is, once the correct positions of the bottom of the die cavity have been found) then cell fabrication is relatively rapid.

The first attempt to make these cells in any way other than the Carver press was by using a 150 ton capacity, manually activated, semiautomatic hydraulic press with a ram size of 2 1/8".

When use of the semiautomatic press was first attempted it was feared that the brittle LiAl alloy anodes might not be successfully sheared. This is important because the 2 1/8" diameter cells had to be cut down to 1" diameter. If

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this were possible then at least two cells could be cut out of the larger ones. As it turned out the anode layer cut well but the catholyte layer did not. The graphite (and perhaps $MoCl_5$) did not compress well and made a very brittle cell. When these cells were cut down the catholyte layer had a tendency to chip off. Also it appeared that the catholyte layer did not adhere well to the anolyte layer, and the cell easily delaminated during the cut down process. This was less of a problem when the cell was subjected to less pressure and when the catholyte contained smaller proportions of $MoCl_5$ and graphite. A similar problem was encountered during the second single cell study and will be commented upon later. Shaving dies were resharpened and reshaped, and ultimately a die was found which produced good cells but with relatively ragged edges. These were the cells used to make battery #10, the 28 volt battery.

Batteries #12, #13, and #14 constituted a series made to investigate the ability of the battery to function over the temperature range of $-54^{\circ}C$ to $+74^{\circ}C$. Battery #12 was the room temperature test and served as a control sample for the other two. This battery had a quite typical voltage and activation time. The lifetime was somewhat better than expected. The internal resistance was also a little better than expected but the battery was sufficiently typical to be a good control unit. Battery #13 was the hot unit. This battery was heated to $74^{\circ}C$ for three hours prior to testing. It was removed from the oven and tested in less than one minute so that the internal temperature would not deviate much from the desired $74^{\circ}C$.

Experience provided by battery #2, which was put in an oven to "burn off" the high voltage peak, showed that the battery was in the oven for almost 5 minutes before any appreciable change was noted in the voltage. Later examination of battery #20, (which contained a thermocouple) showed that it took nearly five minutes before the internal temperature changed by one C°. Therefore, it was felt that after

removal from a hot oven the internal temperature would not change appreciably in one minute.

Battery #14 was the cold battery. This battery was cooled for three hours in a chamber at -54°C. Again it was tested within one minute after removal from the chamber so that the internal temperature might truly be -54°C. The hot battery performed as expected. It had a slightly higher voltage (11.3 volts). However, the lifetimes and energy densities were slightly lower than expected. The cold battery had a very low voltage and very short life. That is, the voltage was only 4.3 volts and the energy density to 50% was 2.06 whr/lb. The post mortum examination of the cell stack showed no obvious reason for this unexpected low performance.

From the results of these three batteries it was concluded that either the electrochemical system would not operate over this temperature range or else the 120 cal/in^2 heat paper was not satisfactory. So, batteries #15 and #16 were made with 140 cal/in^2 heat paper.

Batteries #15 and #16 performed quite well. Battery #15 was the cold battery, which produced a voltage of 10.8 volts and a lifetime of 80% of 54 seconds. Battery #16 was the hot one, and it produced a voltage of 10.4 volts and an 80% lifetime of 74 seconds. The results of these tests demonstrated that the electro-chemical system was certainly capable of working throughout this temperature range. The problem with #14 was thought to be most likely the wrong calorie value of the heat paper. But since earlier battery testing had showed that 120 cal/in^2 was probably a good heat value, another battery was made with 120 cal/in^2 heat paper. This was battery #19.

Battery #19 was intended to be an exact duplicate of #14. It was cooled for three hours to -54°C prior to testing. This battery had a voltage of 10.6 volts
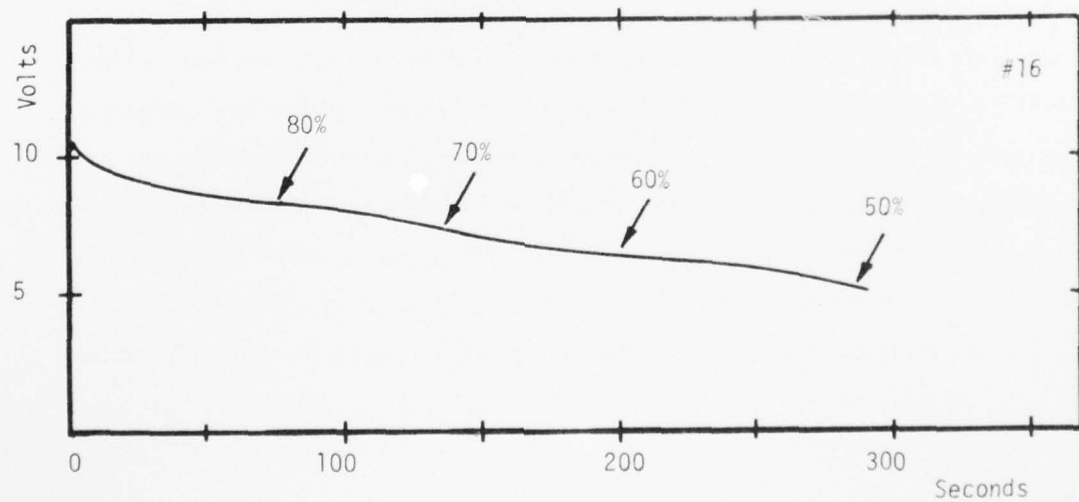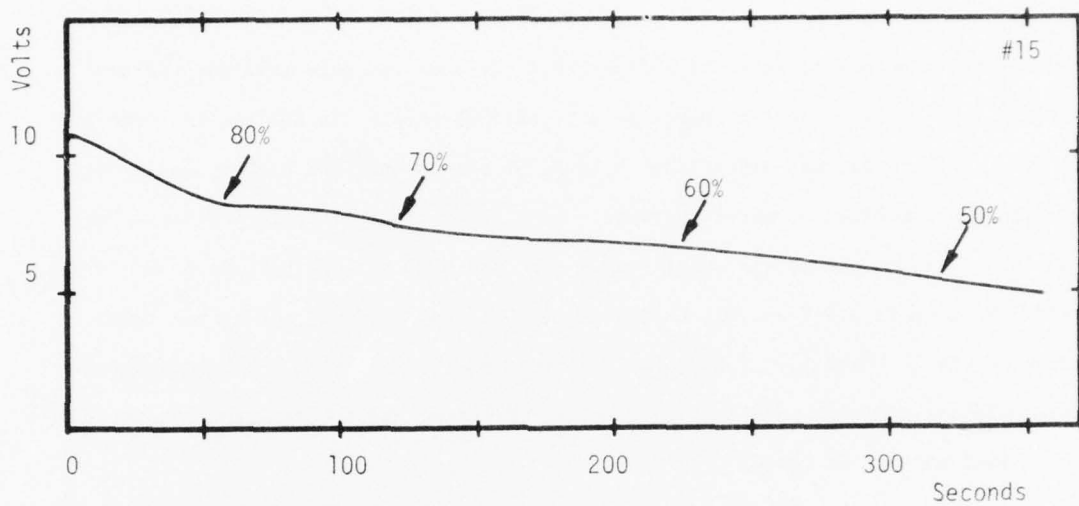
FIGURE 14 A_L/C_{L_2} BATTERY DISCHARGE CURVES (BATTERIES #15 & 16)

and a surprising 80% lifetime of 153 seconds. In some respects this was the best battery made so far, with an energy density of 10.9 whr/lb. to 80% and 22.1 whr/lb. to 50%. Battery #19 was significant because it showed that the battery really did work in the specified temperature range. Also, the output of battery #19 was very similar to the output of the single cells that had had the high voltage peak "burned off". Yet, battery #19 was not heated at all but was, in fact, cooled for three hours to -54°C. That is, it had been felt that energy densities of this magnitude were only available through the "burning off" process, and the results of battery #19 showed this to be false.

It can be concluded from the combination of results of batteries #12, #13, #14, #15, #16 and #19 that the $Al/NaAlCl_4/MoCl_5$ battery will perform within the specified temperature environment of -54°C to 74°C.

Batteries #17 and #20 were each built with a thermocouple inside so that the internal operating temperature might be accurately measured. Battery #17 produced a voltage of 10.2 volts and a 50% life of greater than 420 seconds, but the thermo-couple part of the experiment was unsuccessful. The thermocouple had been welded to two of the terminals on the underside of a battery header. The battery header was then soldered on, and more thermocouple wire was fastened to the terminals on the upperside of the header. These were attached by crimping into a solderless connector and soldering the connector to the terminals. This proved to be an unsatisfactory design because of potential differences created at these connection points. The battery was fired and the data recorded, but the thermocouple data were not valid.

Battery #20 was made by drilling a narrow hole through one terminal and passing the thermocouple lead through this hole. The hole was then sealed with an epoxy. The thermocouple performed satisfactorily. The battery was conditioned by storing in a chamber at -53°C for three hours, after which time the thermocouple

MICROCOPY RESOLUTION TEST CHART

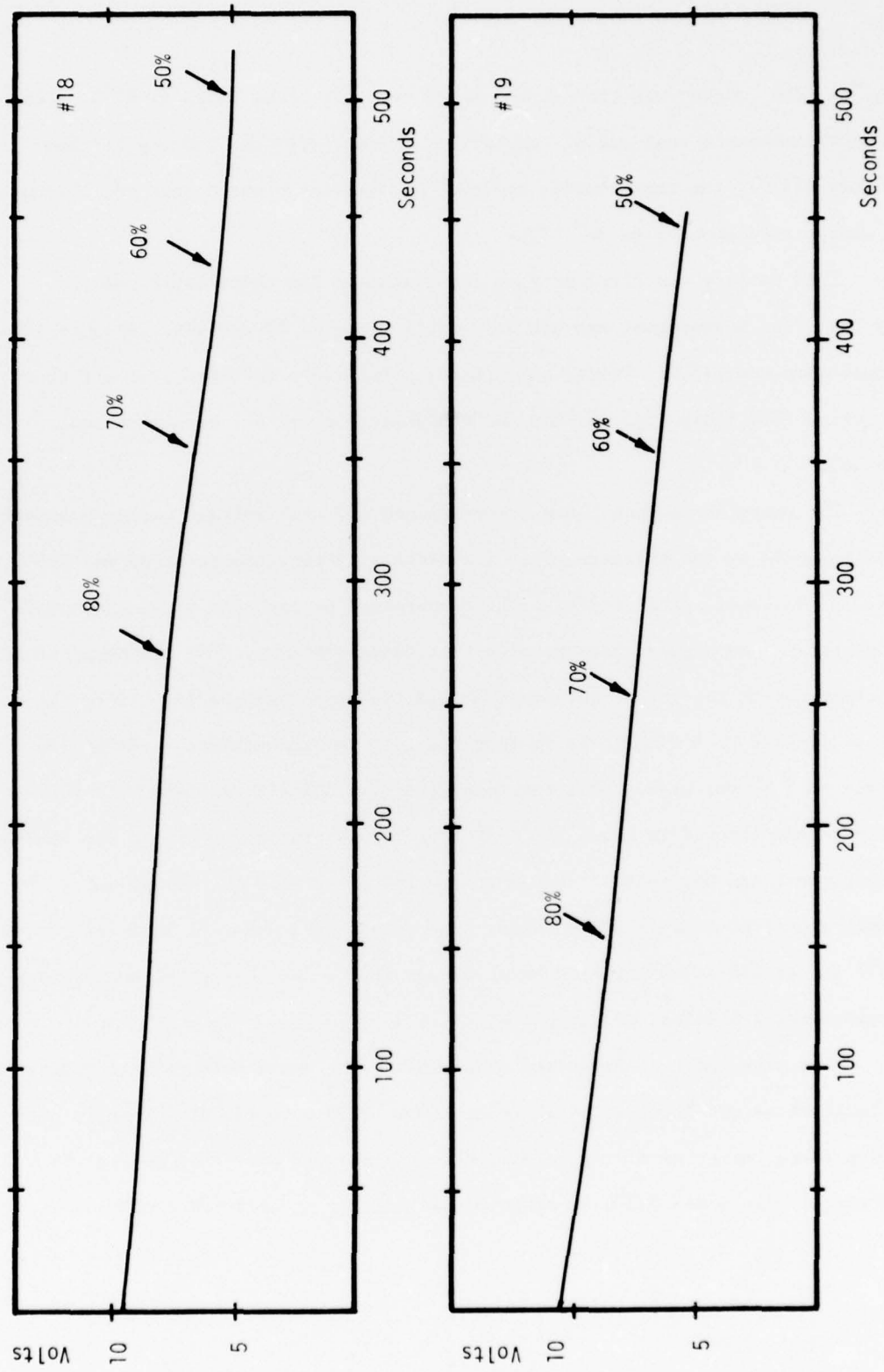NATIONAL BUREAU OF STANDARDS-1963-A
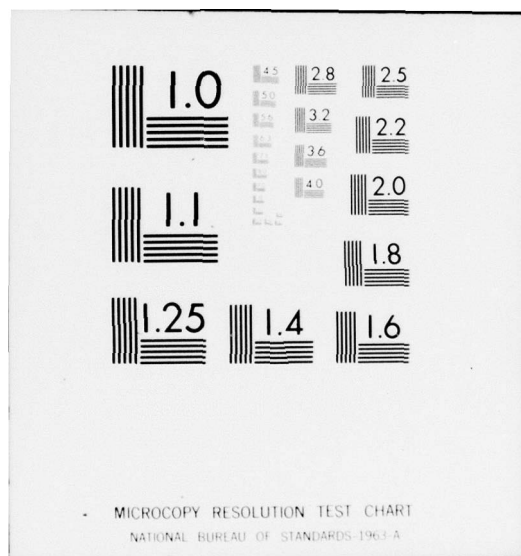
FIGURE 15 A_L/C_{L_2} BATTERY DISCHARGE CURVES (BATTERIES #18 & 19)

read -48°C. The battery was then stored in an oven for three hours at 97°C, after which the thermocouple read 100°C. The following day, with the battery at room temperature (27°C), the thermocouple read 30°C. Thus it appeared that the thermocouple always read about 3 to 5C° high.

This battery was fired at room temperature. The temperature rose so quickly the first measurement was not made until time t = 10 seconds. At this time the temperature was 295°C. Twenty temperature points were recorded over a fifteen minute period (See Table 13). A time and temperature curve has been sketched. (Figure 16).

The temperature when the battery reached 80% peak voltage was approximately 165°C as measured by the thermocouple. The highest temperature recorded was 295°C, measured at 10 seconds after firing. The temperature during this first 10 seconds was undoubtedly even higher, because when this measurement was made the temperature was falling. Since the three "calibration" temperatures taken before firing the battery were all 3 to 5 C° high it is felt that all the temperature readings are probably 3 to 5 C° too high. Thus the temperature at 80% life was 160°C to 162°C. This temperature dropped to about 138°C at 50%. At 465 seconds the load was removed from the circuit and the voltage jumped to 7.0 volts and held this level until the experiment was terminated at 920 seconds. The temperature when the load was removed was 135°C and at 920 seconds the temperature was 116°C. At this point the battery still maintained 7.0 volts, measured with no load.

This experiment demonstrated that the battery would perform satisfactorily over a temperature differential of at least 160 C° (295°C to 135°C). This is not surprising since batteries #12, #13, #14, #15, #16 and #19 performed over a -54°C to 74°C range. Since the 295°C temperature was not the highest temperature (only

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TABLE 13

TIME VS. TEMPERATURE

	TIME	TEMP ($^{\circ}$C)		TIME	TEMP ($^{\circ}$C)
T_0	0	85	T_{11}	274	144
T_1	10	295	T_{12}	324	142
T_2	42	209	T_{13}	407	140
T_3	66	190	T_{14}	468	139
T_4	88	181	T_{15}	588	137
T_5	107	174	T_{16}	670	133
T_6	126	167	T_{17}	802	127
T_7	144	162	T_{18}	888	122
T_8	166	157	T_{19}	920	120
T_9	195	152			
T_{10}	239	147			
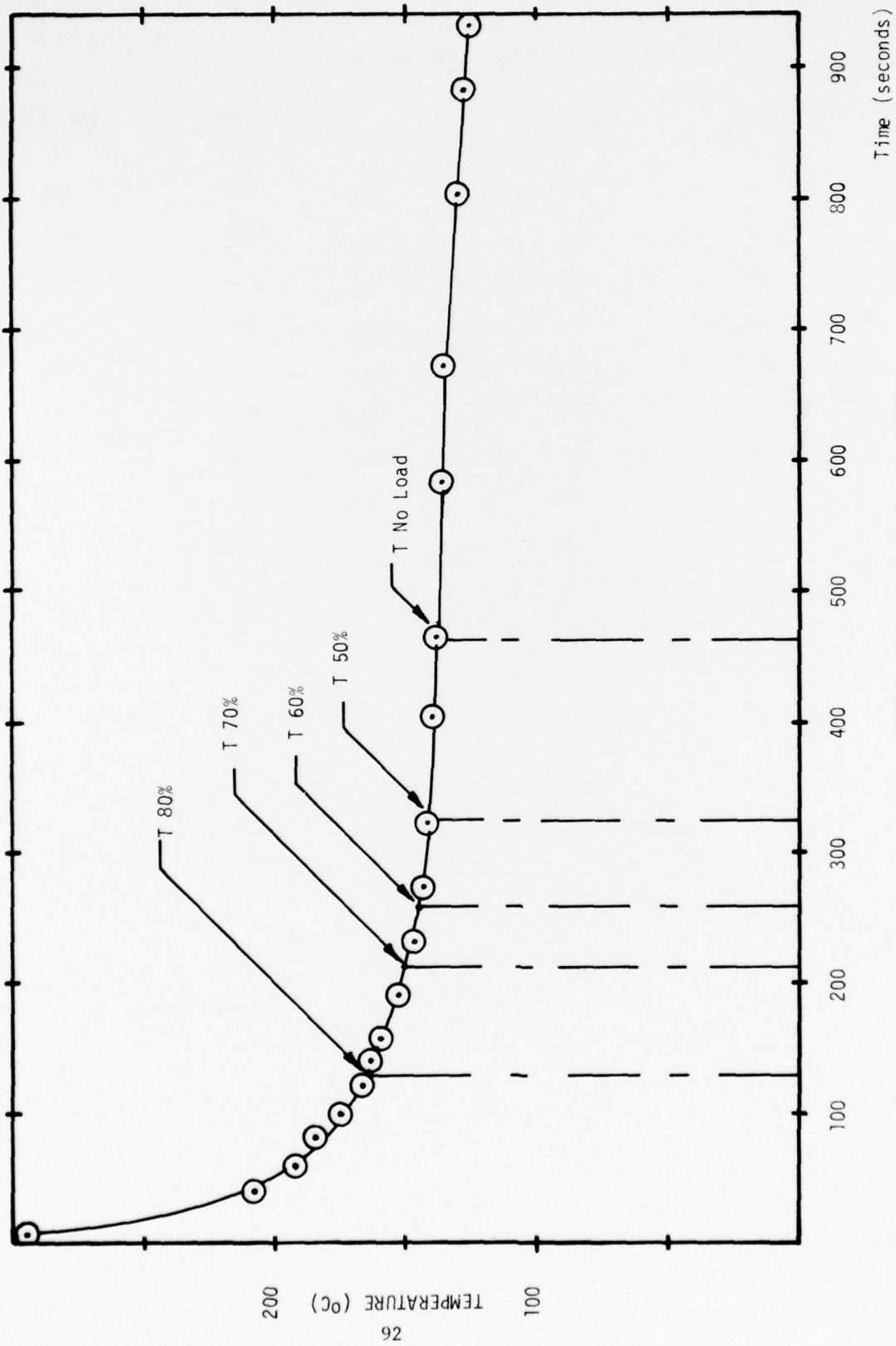
FIGURE 16. TEMPERATURE VS. TIME

the highest recorded) it can be concluded that the useful temperature range for this electrochemical system is greater than 160 C^O.

Battery #18 was made using heat pellets instead of heat paper. The best pellets were made from iron/potassium perchlorate mix, heat powder, 88-12, received from General Electric Company, Nuclear Devices Department by way of Sandia Research Laboratories. This material is composed of 88% iron and 12% potassium perchlorate.

The pellets were prepared on the semiautomatic press at a pressure of 30 tons on the 2 1/8" die. A target value of 120 cal/in^2 was used. However, the finished pellets had a average weight corresponding to 109.3 cal/in^2. This difference is due to the ragged edges of the cut down pellets. The pellets were about 1/32" thick and were very flexible.

The cells of the battery weighed 2.183 grams when cut down. The cell formula for this battery (and for all batteries, #12 thru #20) was as follows:

$$Anode = 17.5 \; ^W/o$$

$$Anolyte = 25.0 \; ^W/o$$

$$Catholyte = 57.5 \; ^W/o$$

The catholyte formula was (for batteries #12 thru #20) as follows:

$$NaAlCl_4 = 26.12 \; ^W/o$$

$$MoCl_5 = 58.05 \; ^W/o$$

$$Graphite = 15.83 \; ^W/o$$

The 80% life of battery #18 was 269 seconds with an energy density of 14.8 whr/lb. The 50% life was 500 seconds and had an energy density of 21.7 whr/lb. The 80% energy density of 14.8 whr/lb. was greater than for any battery made at this point, and was even better than any single cell tested (S.C. #67 was the best with 10.2 whr/lb. to 80%). It should be pointed out that no attempt to "burn off" the high voltage peak was made. The voltage was an atypically low, 9.4 volts. The low

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voltage and the long activation, were attributed to the 110 cal/in^2 heat value of the pellets. However, a _post mortum_ examination of the battery showed that one of the six stack heat pellets did not burn at all. Despite the low calorie value of the pellets, and despite the fact that one of six pellets did not fire, this battery still had the best energy density of any of the tests made so far.

Battery #21 was also made with the Fe/KClO$_4$ heat source. Since the heat source is a good conductor both before and after firing it was felt that cell connectors were not needed.

Battery #21 was made with double two-layer cells. That is, the cells were made from two two-layer disks. See the discussion of Single Cell #68.

The fired battery had a peak voltage of 21.7 volts and a peak current of 1.447 amps. The battery contained 2 1/8" diameter cells (not 1" diameter as all the others had) so the current density was 63 mA/cm^2. The activation time was 2.32 seconds. This slow activation and low voltage (1.55 volts/cell) suggested that some of the heat disks failed to ignite. In about 20 seconds the battery voltage had dropped to 17.8 volts (about 82%) and then started to rise again to a new peak of 21.9 volts at about 100 seconds. After 114 seconds the battery shorted out. The actual drop from 21.9 volts to zero took about 30 seconds. The battery case became hot enough to melt the solder around the header, and the battery vented. It was removed from the laboratory and set in a few inches of water for cooling. The battery produced 3.4 whr/lb before shorting out. Because so much heat was formed, it was believed that the catholyte oxidized the remainder of the iron in the heat source. Apparently the catholyte and Fe/KClO$_4$ heat disk cannot exist in direct contact.

It should be noted that the cells (that is, the two layer disks) were stored for about three days before use and that they showed no signs of machanical deterioration. The catholyte layers did appear to have taken on a slight reddish cast.
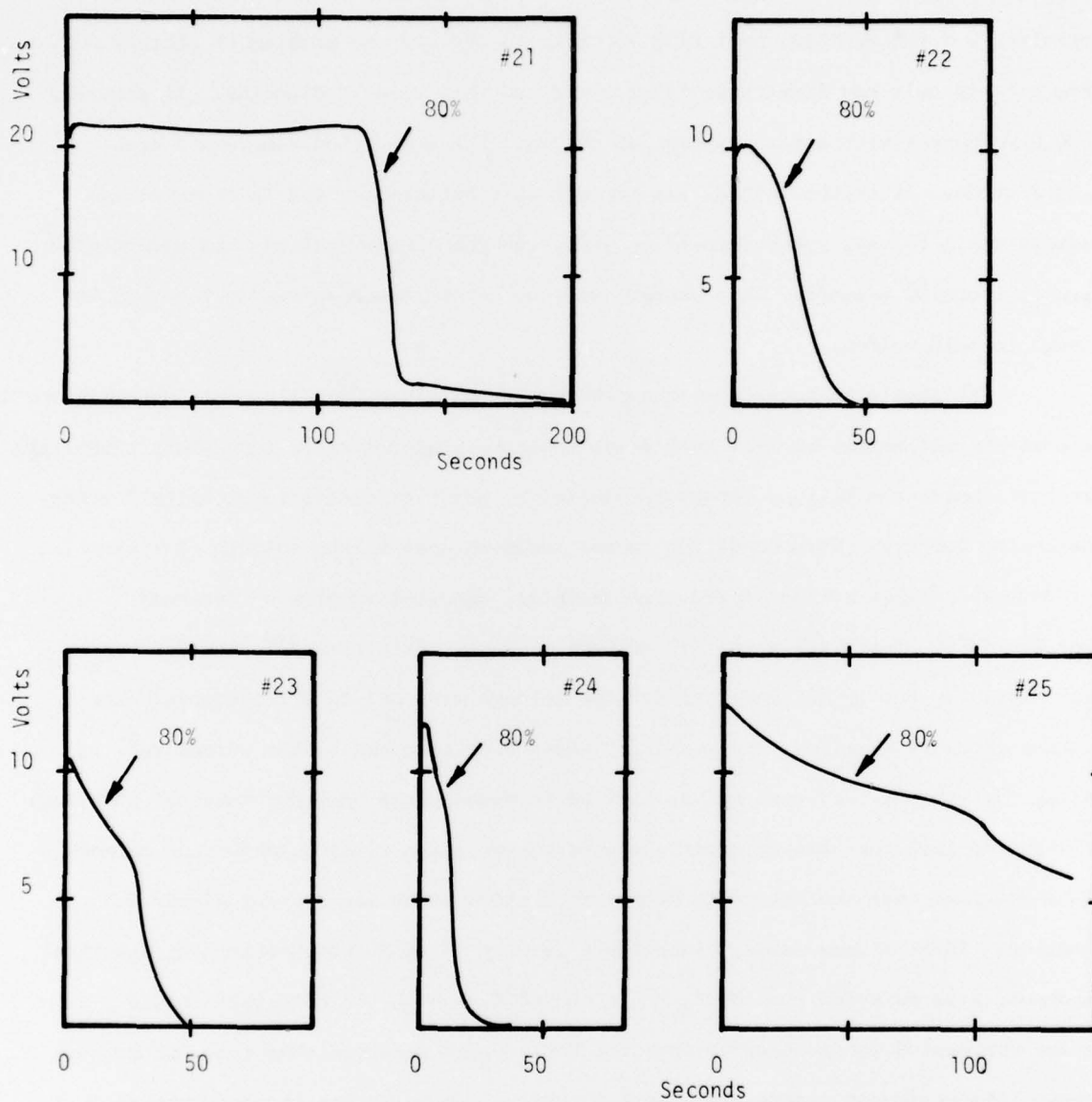
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FIGURE 17 A_L/C_{L2} BATTERY DISCHARGE CURVES (BATTERIES #21, 22, 23, 24, & 25)

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Battery #22 was made with a nickel disk, 0.004" thick, between the catholyte and the $Fe/KClO_4$ heat disk in order to obviate the problem of battery #21. This battery only had five three layer cells and they were 1" diameter. It produced a 10.0 volt peak with a peak current of 667 mA. The activation time was a slow 1.23 seconds. After the initial six seconds this battery started to lose voltage rapidly until 80% was reached in 17 seconds, and the battery voltage was essentially zero in about 50 seconds. This battery was too hot to touch but did not become hot enough to melt solder.

It should be noted that these batteries have been described as "shorting out". In most thermal batteries this term means that the electrolyte or some other conducting material inside the battery causes an electrical short circuit across the cell stack inside the battery. This condition causes rapid changes in the voltage (for example, a 10% or 20% change in just a few milliseconds). Another symptom of internal shorting is an electrically "noisy" voltage readout. Batteries #21, and #22 were both "noisy". But in neither case did the voltage drop off in milliseconds. The voltage drops were severe, and were very rapid when compared to the normal rate of voltage drop, but they were not as fast as is usually the case for internal shorting. It appeared that the battery materials were consumed ten times quicker than normal. It is possible that the catholyte became so fluid that it was causing electrical shorting. This is reasonable, since there is only 2% or 3% Cab-O-Sil in a catholyte. It should also be noted that $MoCl_5$ boils at $268^{O}C$, and if the catholyte should become overheated it is possible that the $MoCl_5$ could vaporize away from the cathode area. This would not necessarily cause electrical shorting but it would appear that the catholyte was being consumed faster than it really was.

Battery #23 was similar to #22 except that the heat disks were placed in cell connectors instead of just having a nickel disk between the heat disk and catholyte.

The construction of #23 was actually quite similar to #18. The peak voltage was 10.9 volts and the peak current 727 mA. The current density was 143 mA/cm^2, and activation was 1.18 seconds. The 80% life was 14 seconds and the battery quickly died to 50% in the next 16 seconds. However, the battery was cool enough to hold in the hand.

Battery #23 contained three extra cells. Two of these were tested with the single cell tester. Refer to the results of Single Cells #70 and #71.

The post mortum examination of #23 showed areas in the side of the stack where the battery material had flowed. This is contrasted with the post mortum of #21 where the battery stack was fused into one solid mass, or #22 where the cells were fused together and had to be broken apart. In #23 the cells could still be separated except where they had fused together at the "hot spots".

It should be recalled that in Battery #18, the first battery made with Fe/KC10$_4$ heat disks, one of the heat disks failed to ignite. The fuze strips were changed to 235 cal/in^2 to aid in the heat disk ignition of Batteries #21, #22, and #23. It was felt that possibly these hotter fuze strips were responsible for the "hot spots" along the edge of the stack. Therefore, Battery #24 was made similar to #23 except that 170 cal/in^2 fuze strips were used instead of 235 cal/in^2 strips.

Battery #24 had a peak voltage of 12.7 volts and a peak current of 847 mA. The current density was 167 mA/cm^2 and the activation was 0.32 seconds. The 80% life was 8 seconds and the readout was very noisy. The battery did not get excessively hot but the stack did fuse together.

Another possible source of this difficulty could be an anolyte with an incorrect amount of Cab-O-Sil. The amount of Cab-O-Sil in the anolyte being used could not be determined, and so a new anolyte was ground and used to make a new catholyte. These two new powders, the anolyte and catholyte, were used in all batteries from #25 thru #30.

Battery #25 was identical to #24 except that the cells were made from the new powders. The heat source was the $Fe/KClO_4$ disks. The peak voltage was 12.4 volts and the peak current was 827 mA. The current density was 163 mA/cm^2 and the activation was 0.40 seconds. The 80% life was 49 seconds and the 50% life 134 seconds. This made the 80% energy density 5.13 whr/lb. and the 50% energy density 10/21 whr/lb.

The performance of this battery was similar to #7, #8 or #9. It had a relatively high peak voltage, as did batteries #24 and #25. This was similar in behavior to one of the high voltage "spike" single cell tests.

Battery #26 contained 120 cal/in^2 heat pads instead of $Fe/KClO_4$ heat disks. In effect, the only difference in this battery and many of the earlier batteries was the anolyte and catholyte. That is, performance similar to Batteries #4, #12, or #19 was expected. However, Battery #26 had a peak voltage of 12.8 volts and a peak current of 853 mA. The current density was 163 mA/cm^2 and the activation was 0.36 seconds. The 80% life was only 7.7 seconds and the 50% life only 26.1 seconds. The voltage trace was very noisy. The cell stack showed "hot spots" and the cells were fused together.

In an attempt to remedy this flow of the anolyte and catholyte a portion of each powder was mixed with kaolin. The anolyte was mixed with 10% kaolin and the catholyte had 30% kaolin added. The kaolin was mixed in only mechanically, and no attempt was made to fuse either powder. Cells were then made and these assembled into Battery #27.

Battery #27 had a peak voltage of 11.6 volts and a peak current of 773 mA. The current density was 153 mA/cm^2 and the activation was 0.63 seconds. The 80% life was 62 seconds and the 50% life was 126 seconds. The battery produced 5.8 whr/lb. to 80% and 8.9 whr/lb. to 50%. The overall performance of Battery #27 was very similar to that of #25.
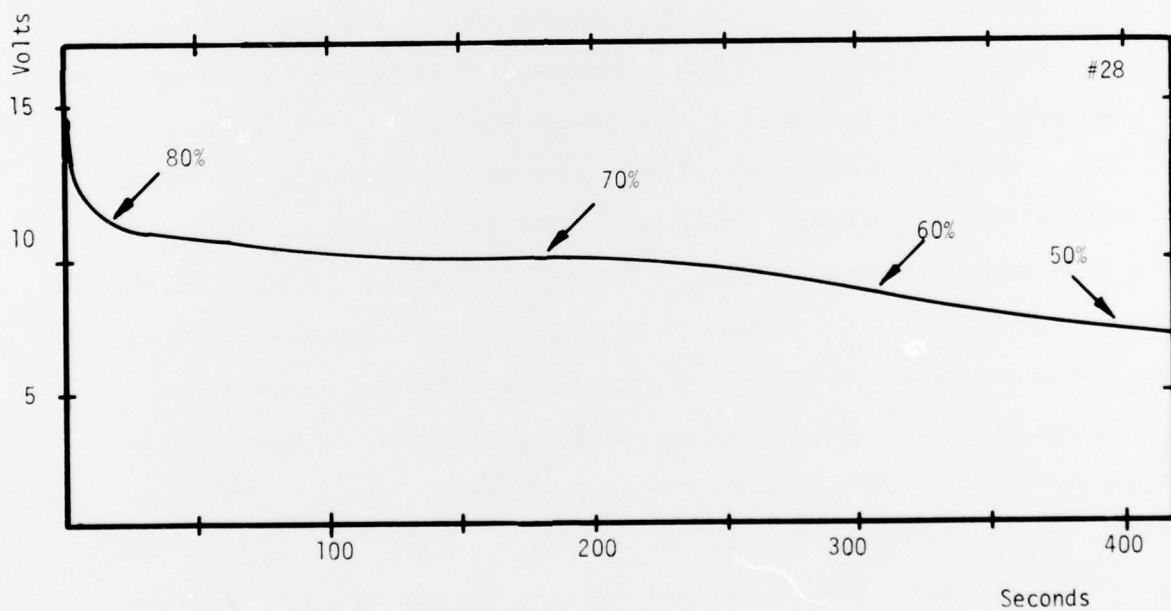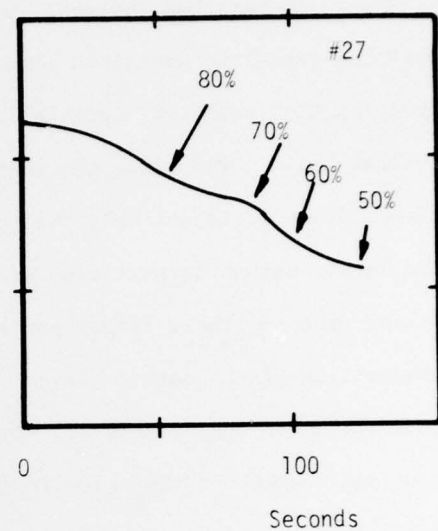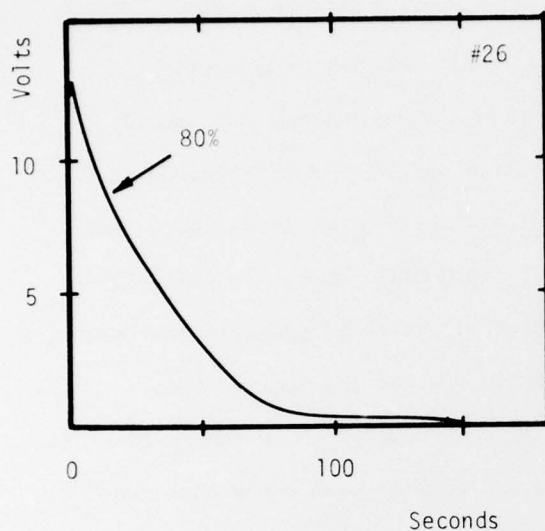
FIGURE 18 A_L/C_{L_2} BATTERY DISCHARGE CURVES (BATTERIES #26, 27 & 28)

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It was observed while mixing kaolin into the catholyte and anolyte, that the catholyte contained some large sized particles. Further observation revealed that catholyte material that would pass thru a #80 sieve one day, would not pass thru a #40 sieve the next day. The catholyte particles had increased in size. Since it is unlikely that the graphite crystals would grow, it was felt that the larger catholyte particles were rich in $NaAlCl_4$ or $MoCl_5$. Since, in the cell making process, these larger particles were raked off it is quite possible that the composition of the cathode layer of some of the cells was not the same as the composition of the catholyte. Also, it is possible that some of these larger particles were not "raked off" but were instead pushed into the cell in such a way that the anolyte layer was penetrated and the anode and cathode layers were in direct contact with each other. This, of course, is an electrical short, and the result would be a shorter useful life accompanied by the production of heat from the resulting redox reaction. For this reason it was made a standard practice to always grind and sieve the catholyte material just prior to cell fabrication.

In order to determine the relative magnitude of internal energy losses, Battery #28 was made and tested with a 50 ohm load. It was otherwise identical to #25. This battery had a peak voltage of 14.5 volts and a peak current of 290 mA. The current density was 57.2 mA/cm^2 and the activation was 0.29 seconds. The 80% life was 15 seconds but the 50% life was 397 seconds. The performance of this battery was identical to one of the high voltage spike single cell tests. The energy density to 80% was only 0.64 whr/lb. but the energy density to 50% was 9.8 whr/lb. The readout was not "noisy".

Batteries #21 thru #28 were all made with the same cell formula:

$$\text{Anode} - 0.350 \text{ gm} = 17.5 \text{ }^w/o$$

$$\text{Anolyte} - 0.500 \text{ gm} = 25.0 \text{ }^w/o$$

$$\text{Catholyte} - 1.150 \text{ gm} = 57.5 \text{ }^w/o$$

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The catholyte formula for Batteries #21 thru #30 was (except #27):

$$NaAlCl_4 = 26\ ^w/o$$
$$MoCl_5 = 58\ ^w/o$$
$$Graphite = 16\ ^w/o$$

These formulas were picked as a result of the single cell factorial study. It was decided to increase the weight of the anolyte layer slightly in order to prevent internal cell shorts. Hence the cell formula was changed to:

$$Anode = 15\ ^w/o$$
$$Anoltye = 30\ ^w/o$$
$$Catholyte = 55\ ^w/o$$

Cells with this formula were made and assembled into Battery #29.

Battery #29 was also tested with the 50 ohm load. The peak voltage was 11.4 volts and the peak current was 228 mA. The current density was 45 mA/cm^2 and the activation was 0.35 seconds. The 80% life was 310 seconds and the 50% life was 900 seconds. This battery produced an energy density of 8.3 whr/lb. to 80% and 15.4 whr/lb. to 50%. The readout of this battery was not at all noisy.

Battery #30 was similar to #29 except larger. This battery was built with eleven cells, 1.914" diameter. The heat source was 120 cal/in^2 Fe/KC10$_4$ heat disks. The battery case was 3 3/8" tall and 2 5/8" in diameter. This case was approximately 40% full of active materials (cells and heat source). The remainder of volume was filled with sheet asbestos. The peak voltage of this battery was 28.2 volts and the peak current was 806 mA (a 35 ohm load was used). The current density was 43.4 mA/cm^2. Due to a recorder failure the activation time was not recorded, but was observed to be less than one second. The 80% life was 362 seconds and the 50% life was 754 seconds. Battery #30 produced 10.4 whr/lb. to 80% and 16.7 whr/lb. to 50%. The voltage readout was not at all noisy. The fired battery was cool enough to be held in a bare hand.
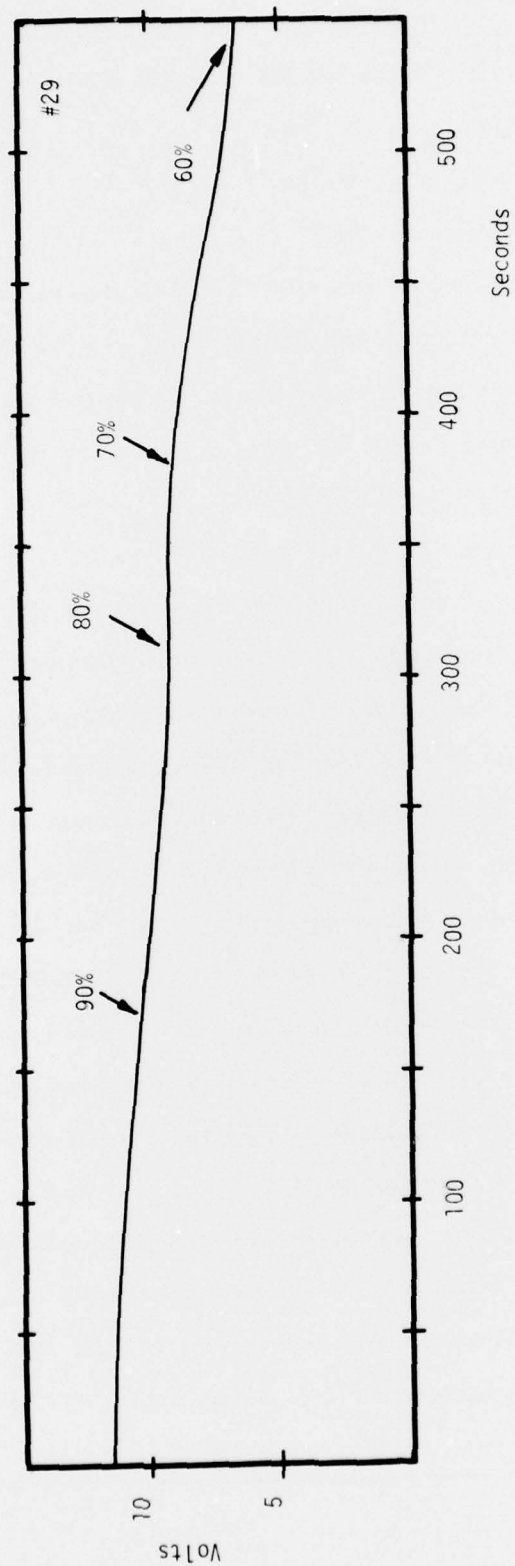
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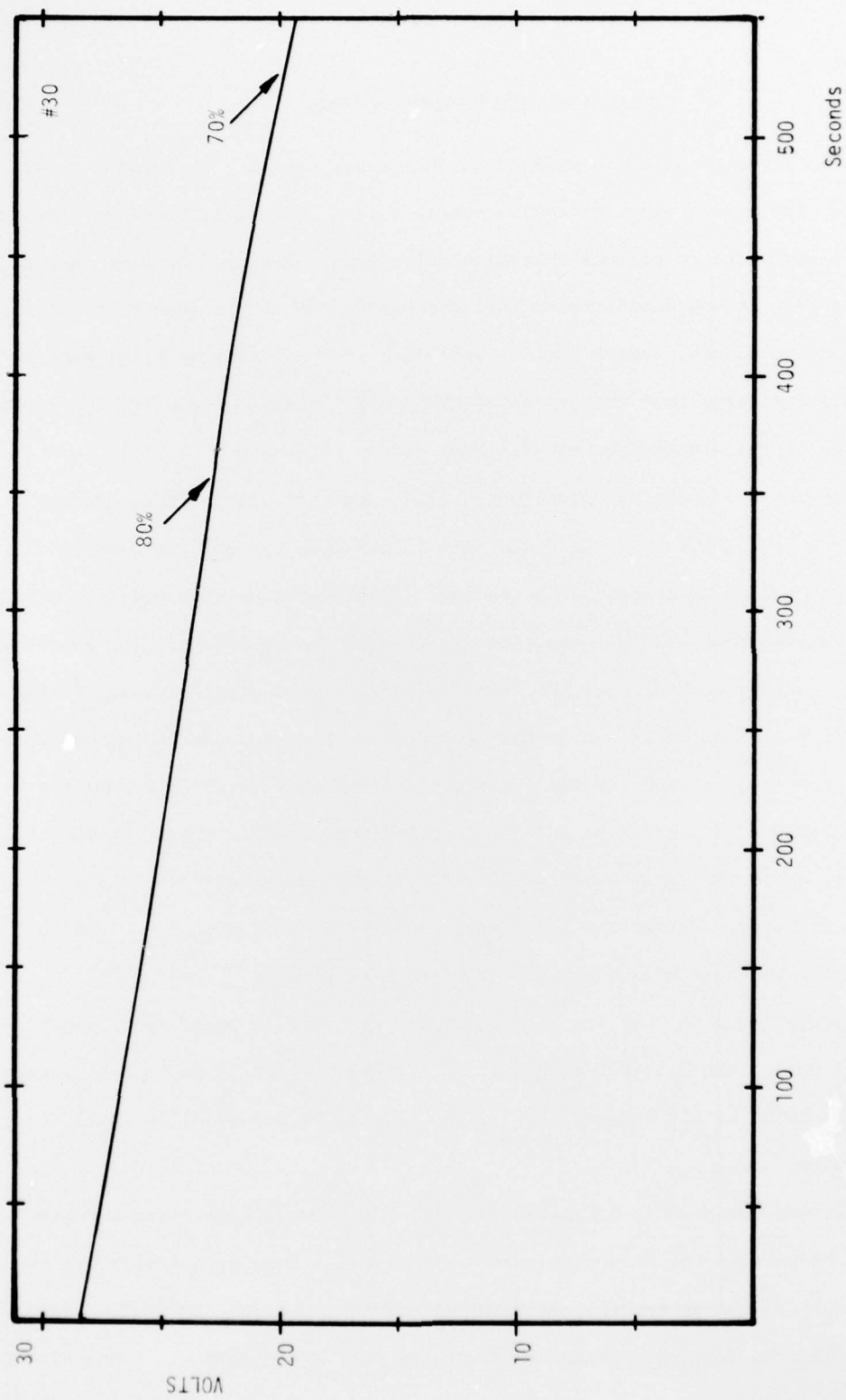FIGURE 19. A_L/C_{L_2} BATTERY DISCHARGE CURVE (BATTERY #29)

FIGURE 20. A_L/C_{L_2} BATTERY DISCHARGE CURVE, (BATTERY #30)

SECTION III

CONCLUSIONS AND RECOMMENDATIONS

The first problem encountered at Eureka was the lack of large amounts of $NaAlCl_4$. For making experimental batteries a good batch size would be five to ten pounds. In order to produce this material a large pressure container needs to be designed. It was demonstrated that the $NaAlCl_4$ which was made by relatively crude methods at Eureka, worked just as well as the high purity material made at FJSRL. This indicates that the expensive high purity raw materials and the lengthy purification of the electrolyte material may not be necessary.

A pressure reaction vessel would also make it possible to experiment more with the $AlCl_3/NaCl$ mix. It would make it possible to vary the amounts of either component and to change the percentage of Cab-O-Sil as necessary. A pressure vessel would also make possible experimentation with the catholyte. It was noticed late in the battery testing that the catholyte crystals apparently grew. Perhaps this problem would not be as bad if the catholyte were fused. It may be possible to fuse a percentage of MoO_3 in the catholyte. It may be possible to fuse the $NaAlCl_4$, Cab-O-Sil, and graphite and then add $MoCl_5$ or fuse in MoO_3. Fusing, followed by grinding, would also provide a control of the particle size of the catholyte. This would probably make the catholyte more compactable and this could lead to a cell that is easier to shear and which can withstand more physical handling.

It was noticed that the LiAl alloy did not seem to smear along the side of the cell during the cell making process. If this is true it may not be necessary to shear the cells at all because they may be able to be pressed into their final size and shape.

It was observed during single cell testing that a high voltage "spike" was often observed in the discharge curve of the cell. Similar behavior was observed in the battery discharge curves. At first it was believed that this was a random phenomenon but the factorial design study showed that the height and shape of this

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"spike" was a function of the cell formula. Other single cell experiments showed that the "spike" would change shape with the temperature of the cell. Since this "spike" could seriously interfere with the reliability of a production battery more work must be done to discover the cause of the "spike" and to discover some method of controlling the size and shape of the "spike".

Some interesting problems were encountered when battery fabrication began. As has already been mentioned these cells are hard to shear. For this reason special cutting dies had to be designed. Also, the LiAl alloy was dusty material and this dust is a considerable respiratory irritant. The $MoCl_5$ catholyte was also a noxious material. Special methods of handling these materials will have to be developed before these batteries can become a production item.

The remainder of the battery construction was not too difficult. The goals of a fully engineered battery include a nominal voltage of 28 volts and a current of about 2 amps. This was done with Battery #11.

Another of the goals of a fully engineered battery is an operating life of 45 minutes. This, when considered in conjunction with the one pound maximum weight requirement, corresponds to an energy density of 42 whr/lb. The highest energy density observed by any battery was about 15 whr/lb. This is about one third of the required energy density and corresponds roughly to a 15 minute battery. This is a good improvement over existing thermal batteries. The longest actual life observed was 6 minutes. It should be noted that these energy density figures only include the weights of the cells and the "true" energy density of a battery will be much lower than the figures quoted here. However, Battery #30 still produced a peak voltage of 28 volts across a 15 ohm load and required 362 seconds to reach 24 volts. Battery #30 only contained one series stack of eleven cells.

It is felt that this work has proven that this is a relatively long life battery and that the requirements for a fully engineered battery are quite realistic.

Of the thirty battery tests made fourteen activated in over one second. Out of the last seven batteries tested none had an activation greater than 0.63 seconds. Therefore, it appears that the activation requirement is not going to be a problem with this battery. Electrical noise was noted in only a few cases and it is not felt that the noise requirement is going to be a problem.

Battery tests #12 thru #17 proved that the battery will function well between the required temperatures of $-54^{\circ}C$ to $74^{\circ}C$. While no exact measurements were made of the skin temperature these batteries were often cool enough to be held in the hand without any protection and it is felt that the skin temperature requirement is realistic and attainable.

It is possible to make a battery with a volume less than six cubic inches or a weight of less than one pound. However, the energy density and current density measurements demonstrate that a battery that size would probably not have a very long life (less than ten minutes). To make a battery that would produce the required voltage and amperage for the required time would take a battery of about three times the recommended weight and perhaps double the recommended volume. In any case an optimized energy density would require more engineering to reduce wasted space and weight.

One suggestion which immediately presents itself to this battery is a lightweight plastic case. This is a real possibility considering the low operating temperature of this battery.

No batteries were tested in an environment of acceleration, shock or vibration. Since flow of the electrolyte was observed in some of the static tests performed it is felt that the optimum antiflow properties of the cell have not yet been attained and more engineering needs to be done before testing of the nature is begun.

In summary the Eureka Advance Science Corporation used an electrochemical cell developed by Frank J. Seiler Research Laboratory to make a thermal battery which has all of the operating characteristics of existing thermal batteries plus the advantages of a cooler operating temperature, and a much longer life. It is felt that this battery has a good utility potential and more work should be done until a fully engineered battery is realized.

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